# Nickel-Catalyzed Enantioconvergent Borylation of Racemic Secondary Benzylic Electrophiles

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## Supporting Information

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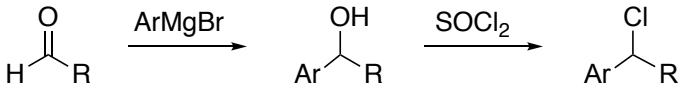
## I. General Information

Unless otherwise noted, reagents were used as received from commercial suppliers. All reactions were performed under an atmosphere of dry nitrogen. Anhydrous chloroform, 1,2-dimethoxyethane (DME), and cyclopentyl methyl ether (CPME) were purchased from Sigma-Aldrich and stored under nitrogen. Other solvents were purified by passage through activated aluminum oxide using a solvent-purification system.

NMR spectra were recorded on a Bruker spectrometer with a Prodigy broadband cryoprobe (400 MHz for $^{1}H$ and 101 MHz for $^{13}C$); chemical shifts (δ) are reported in ppm downfield from tertramethylsilane, using the solvent resonance as the internal standard. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm, using a 100 mm path-length cell in the solvent and at the concentration indicated. Mass spectra were obtained on an Agilent 7890A GC-MS system with an Agilent 5975C detector or on an Agilent 1290 UHPLC-LCMS system with an Agilent 6140 detector. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm). IR spectra were recorded on a Thermo Scientific Nicolet iS5 (iD5 ATR) spectrometer by attenuated total refection (ATR).

## II. Preparation of Electrophiles

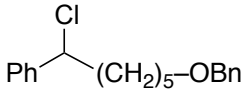
**General Procedure 1 (GP-1): Preparation of racemic secondary benzylic chlorides.**




**Preparation of the benzylic alcohol.** A solution of ArMgBr (1.0 M in THF; 33 mmol, 1.1 equiv;) was added dropwise over 5 min to an oven-dried flask charged with a solution of the aldehyde (30 mmol, 1.0 equiv) in anhydrous THF (40 mL) at 0 °C. Next, the reaction mixture was allowed to slowly warm to room temperature, and it was stirred overnight. Then, the reaction mixture was cooled to 0 °C, and the reaction was quenched by the slow addition of a saturated aqueous solution of $NH_4Cl$ (40 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product.

**Preparation of the benzylic chloride.** Thionyl chloride (2.3 mL, 31.5 mmol, 1.05 equiv) was added dropwise over 2 min to an oven-dried flask charged with a solution of the benzylic alcohol (30 mmol, 1.0 equiv) in $CHCl_3$ (20 mL) at 0 °C (CAUTION: gas formation). Then, the reaction mixture was allowed to slowly warm to room temperature. The progress of the reaction was monitored by GC analysis. After completion, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to provide the desired product.

The yields have not been optimized.




**(6-(Benzyloxy)-1-chlorohexyl)benzene.** The title compound was synthesized according to **GP-1** from 6-(benzyloxy)hexanal[1] and phenylmagnesium bromide, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). 62% yield over 2 steps; colorless oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 8H), 7.35 – 7.29 (m, 2H), 4.88 (dd, *J* = 8.1, 6.4 Hz, 1H), 4.53 (s, 2H), 3.49 (t, *J* = 6.5 Hz, 2H), 2.23 – 2.13 (m, 1H), 2.11 – 2.06 (m, 1H), 1.67 – 1.60 (m, 2H), 1.59 – 1.51 (m, 1H), 1.48 – 1.42 (m, 2H), 1.39 – 1.33 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.9, 138.6, 128.6, 128.4, 128.2, 127.6, 127.5, 126.9, 72.9, 70.2, 63.8, 39.9, 29.6, 26.9, 25.7.

FT-IR (film) 3030, 2936, 1454, 1362, 1102, 696 $cm^{-1}$.

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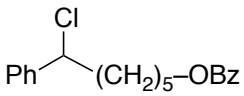
[1] G. Sudhakar, K. J. Reddy, J. B. Nanubolu, *Tetrahedron* **2013**, *69*, 2419–2429.

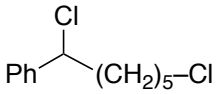



**6-Chloro-6-phenylhexyl benzoate.** The title compound was synthesized according to **GP-1** from 6-oxohexyl benzoate[2] and phenylmagnesium bromide, and it was purified by column chromatography on silica gel (10% $Et_2O$ in hexanes). 74% yield over 2 steps; pale-yellow oil.

$^1H$ NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 4.89 (dd, *J* = 8.2, 6.4 Hz, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 2.25 – 2.14 (m, 1H), 2.12 – 2.04 (m, 1H), 1.84 – 1.75 (m, 2H), 1.68 – 1.58 (m, 1H), 1.56 – 1.48 (m, 2H), 1.47 – 1.39 (m, 1H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 166.6, 141.8, 132.9, 130.4, 129.5, 128.6, 128.4, 128.3, 126.9, 64.8, 63.7, 39.9, 28.6, 26.8, 25.6.

FT-IR (film) 3031, 2941, 1718, 1452, 1274, 1117, 1070, 711 $cm^{-1}$.




**(1,6-Dichlorohexyl)benzene.** The title compound was synthesized according to **GP-1** from 6-chlorohexanal[3] and phenylmagnesium bromide, and it was purified by column chromatography on silica gel (hexanes). 54% yield over 2 steps; colorless oil.

$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 7.36 – 7.32 (m, 1H), 4.88 (dd, *J* = 8.2, 6.3 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.23 – 2.13 (m, 1H), 2.13 – 2.04 (m, 1H), 1.82 – 1.76 (m, 2H), 1.58 – 1.48 (m, 3H), 1.43 – 1.34 (m, 1H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 141.8, 128.7, 128.3, 126.9, 63.6, 44.9, 39.8, 32.4, 26.4, 26.3.

FT-IR (film) 2939, 1493, 1454, 1310, 698 $cm^{-1}$.

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[2] J. E. Wilson, A. D. Casarez, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 11332–11334.

[3] R. J. Fox, G. Lalic, R. G. Bergman, *J. Am. Chem. Soc.* **2007**, *129*, 14144–14145.

## III. Catalytic Enantioconvergent Borylations

**General Procedure 2 (GP-2): Catalytic enantioconvergent borylation.**

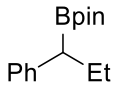
**Preparation of the catalyst.** $NiCl_2$·glyme (15 mg, 0.070 mmol, 10 mol%) and **L1** (33 mg, 0.084 mmol, 12 mol%) were added to an oven-dried 20 mL vial that contained a magnetic stir bar. The vial was capped with a PTFE-lined septum cap, and then it was evacuated and backfilled with nitrogen (3 cycles; caution: light powder, so evacuate and backfill slowly). DME (3.5 mL) was added via syringe, the vial was detached from the Schlenk line, and a nitrogen-filled balloon was attached to the vial. The resulting suspension was stirred at room temperature for 1 h.

**Preparation of a solution of the nucleophile.** An oven-dried 8 mL vial that contained a magnetic stir bar was charged with *t*-BuOK (110 mg, 0.98 mmol, 1.4 equiv). The vial was capped with a PTFE-lined septum cap, and then it was evacuated and backfilled with nitrogen (3 cycles; caution: light powder, so evacuate and backfill slowly). Next, CPME (2.1 mL) was added via syringe, followed by 2-phenylethanol (126 μL, 1.05 mmol, 1.5 equiv). The resulting suspension was stirred at room temperature for 3 min. Under the protection of a flow of nitrogen, $B_2pin_2$ (249 mg, 0.98 mmol, 1.4 equiv) was added quickly to the suspension. The vial was then evacuated quickly (bubbles form) and backfilled with nitrogen (3 cycles). Next, the vial was detached from the Schlenk line, and a nitrogen-filled balloon was attached to the vial. The resulting suspension was stirred at room temperature for 40 min, leading to a colorless viscous solution.

**Enantioconvergent borylation.** The benzylic chloride (0.70 mmol, 1.0 equiv) was added via syringe to the suspension of the catalyst. The resulting mixture was stirred for 5 min, and then the solution of the nucleophile was added via syringe over ~1 min. Next, the balloon was removed, and all of the puncture holes in the septum cap were covered with stopcock grease. The resulting mixture was stirred at room temperature for 3 h.

**Workup.** The reaction mixture was filtered through a short pad of silica gel, eluting with $Et_2O$ (10 mL). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (if the products are exposed to silica gel for an extended period time or are left unpurified for over 12 h, a lower yield may be observed).

**General Procedure 3 (GP-3): Determination of enantioselectivity.** The purified product (~15 mg) was stereospecifically oxidized with $NaBO_3$·$4H_2O$ (~100 mg) in THF/$H_2O$ (1:1; 2.0 mL) at room temperature for 4 h. The mixture was extracted with $Et_2O$ (3.0 mL), the organic phase was dried over anhydrous $Na_2SO_4$, and the volatiles were removed under reduced pressure. The ee of the benzylic alcohol was determined via HPLC analysis, without further purification.




**4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (Table 2, Entry 1).** The title compound was synthesized according to **GP-2** from (1-chloropropyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 141 mg, 82% yield, 86% ee; (*S,R*)-**L1**: 137 mg, 80% yield, 86% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 10.5 min (minor), 12.1 min (major).

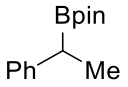
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 4H), 7.08 – 7.02 (m, 1H), 2.14 (t, *J* = 7.9 Hz, 1H), 1.87 – 1.73 (m, 1H), 1.66 – 1.53 (m, 1H), 1.14 (s, 6H), 1.12 (s, 6H), 0.83 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.4, 128.4, 128.2, 125.1, 83.2, 25.8, 24.7, 24.6, 13.9.

FT-IR (film): 2977, 1451, 1371, 1324, 1144, 968, 850, 701 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{15}H_{24}BO_2$: 247.2, found: 247.2.

$[\alpha]^{23}_D$ = +18 (*c* = 1.0, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (Table 2, Entry 2).** The title compound was synthesized according to **GP-2** from (1-chloroethyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 105 mg, 65% yield, 82% ee; (*S,R*)-**L1**: 101 mg, 62% yield, 81% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 11.0 min (minor), 13.5 min (major).

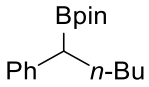
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.20 – 7.12 (m, 1H), 2.46 (q, *J* = 7.5 Hz, 1H), 1.36 (d, *J* = 7.5 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.9, 128.3, 127.8, 125.1, 83.3, 24.7, 24.6, 17.1.

FT-IR (film): 2978, 1459, 1379, 1322, 1144, 844, 701 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{14}H_{22}BO_2$: 233.2, found: 233.2.

$[\alpha]^{23}_D$ = +8.0 (*c* = 1.0, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (Table 2, Entry 3).** The title compound was synthesized according to **GP-2** from (1-chloropentyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 153 mg, 80% yield, 88% ee; (*S*,*R*)-**L1**: 151 mg, 79% yield, 87% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 9.7 min (minor), 10.6 min (major).

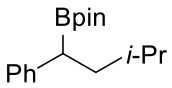
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 4H), 7.08 – 7.01 (m, 1H), 2.21 (t, *J* = 7.9 Hz, 1H), 1.85 – 1.70 (m, 1H), 1.64 – 1.52 (m, 1H), 1.26 – 1.15 (m, 4H), 1.13 (s, 6H), 1.11 (s, 6H), 0.78 (t, *J* = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.5, 128.4, 128.2, 125.1, 83.2, 32.3, 31.6, 24.65, 24.60, 22.7, 14.1.

FT-IR (film): 2979, 1451, 1371, 1323, 1144, 967, 849, 701 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{17}H_{28}BO_2$: 275.2, found: 275.2.

$[\alpha]^{23}_D$ = +18 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylbutyl)-1,3,2-dioxaborolane (Table 2, Entry 4).** The title compound was synthesized according to **GP-2** from (1-chloro-3-methylbutyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 154 mg, 80% yield, 88% ee; (*S*,*R*)-**L1**: 164 mg, 85% yield, 87% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 8.8 min (major), 9.9 min (major).

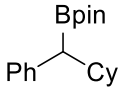
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 4H), 7.08 – 7.01 (m, 1H), 2.34 (t, *J* = 8.1 Hz, 1H), 1.65 – 1.50 (m, 2H), 1.45 – 1.35 (m, 1H), 1.12 (s, 6H), 1.10 (s, 6H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.5, 128.3, 128.2, 125.0, 83.2, 41.5, 26.9, 24.6, 23.0, 22.2.

FT-IR (film): 2979, 1452, 1370, 1323, 1144, 968, 851, 701 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{17}H_{28}BO_2$: 275.2, found: 275.2.

$[\alpha]^{23}_D$ = +26 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.




**2-(Cyclohexyl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 5).** The title compound was synthesized according to **GP-2** from (chloro(cyclohexyl)methyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 136 mg, 65% yield, 78% ee; (*S*,*R*)-**L1**: 120 mg, 57% yield, 77% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 9.9 min (major), 11.6 min (minor).

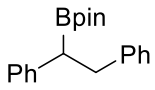
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 4H), 7.18 – 7.10 (m, 1H), 2.06 (d, *J* = 10.4 Hz, 1H), 1.92 – 1.77 (m, 2H), 1.77 – 1.68 (m, 1H), 1.68 – 1.57 (m, 2H), 1.52 – 1.43 (m, 1H), 1.40 – 1.30 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 1.17 – 1.01 (m, 3H), 0.82 – 0.65 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.8, 129.2, 128.0, 125.1, 83.2, 40.3, 33.8, 32.5, 26.6, 26.5, 26.3, 24.7, 24.6.

FT-IR (film): 2978, 1449, 1356, 1319, 1144, 973, 850, 702 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{19}H_{29}BO_2$: 300.2, found: 300.1.

$[\alpha]^{23}_D$ = +9.9 (*c* = 1.0, $CHCl_3$); 78% ee, from (*R*,*S*)-**L1**.




**2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 6).** The title compound was synthesized according to **GP-2** from (1-chloroethane-1,2-diyl)dibenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 164 mg, 76% yield, 82% ee; (*S*,*R*)-**L1**: 176 mg, 82% yield, 84% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 13.3 min (minor), 16.8 min (major).

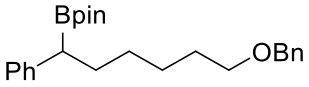
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 8H), 7.08 – 7.02 (m, 2H), 3.07 (dd, *J* = 13.5, 9.8 Hz, 1H), 2.89 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.61 (dd, *J* = 9.8, 6.9 Hz, 1H), 1.03 (s, 6H), 1.02 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.6, 141.8, 128.9, 128.4, 128.3, 128.1, 125.8, 125.4, 83.4, 38.9, 24.6, 24.5.

FT-IR (film): 2978, 1600, 1494, 1370, 1328, 1142, 968, 854, 699 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{20}H_{26}BO_2$: 309.2, found: 309.2.

$[\alpha]^{23}_D$ = +34 (*c* = 1.0, $CHCl_3$); 82% ee, from (*R*,*S*)-**L1**.




**2-(6-(Benzyloxy)-1-phenylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 7).** The title compound was synthesized according to **GP-2** from (6-(benzyloxy)-1-chlorohexyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (10% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 185 mg, 67% yield, 80% ee; (*S*,*R*)-**L1**: 176 mg, 64% yield, 79% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 20.5 min (major), 21.7 min (minor).

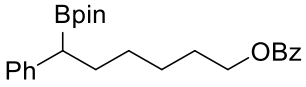
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 4H), 7.33 – 7.29 (m, 1H), 7.28 – 7.21 (m, 4H), 7.18 – 7.13 (m, 1H), 4.51 (s, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 2.32 (t, *J* = 7.9 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.73 – 1.65 (m, 1H), 1.65 – 1.59 (m, 2H), 1.43 – 1.36 (m, 2H), 1.35 – 1.29 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.4, 138.7, 128.4, 128.3, 128.2, 127.6, 127.5, 125.1, 83.2, 72.9, 70.5, 32.5, 29.7, 29.1, 26.2, 24.7, 24.6.

FT-IR (film): 2977, 2932, 1453, 1370, 1323, 1143, 1111, 967, 850, 699 $cm^{-1}$.

LC-MS (ESI) m/z $(M+Na)^+$ calcd for $C_{25}H_{35}BO_3Na$: 417.3, found: 417.3.

$[\alpha]^{23}_D$ = +9.0 (*c* = 1.0, $CHCl_3$); 80% ee, from (*R*,*S*)-**L1**.




**6-Phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (Table 2, Entry 8).** The title compound was synthesized according to **GP-2** from 6-chloro-6-phenylhexyl benzoate and $B_2pin_2$, and it was purified by column chromatography on silica gel (10% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 209 mg, 73% yield, 84% ee; (*S*,*R*)-**L1**: 216 mg, 76% yield, 82% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 12.5 min (major), 13.7 min (minor).

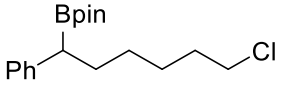
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.03 (m, 2H), 7.63 – 7.55 (m, 1H), 7.50 – 7.43 (m, 2H), 7.29 – 7.21 (m, 4H), 7.19 – 7.11 (m, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.33 (t, *J* = 7.9 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.81 – 1.66 (m, 3H), 1.55 – 1.43 (m, 2H), 1.41 – 1.33 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.2, 132.8, 130.5, 129.5, 128.4, 128.3, 128.2, 125.2, 83.3, 65.1, 32.5, 28.9, 28.6, 26.1, 24.6, 24.5.

FT-IR (film): 2977, 2932, 1720, 1451, 1371, 1323, 1274, 1143, 1115, 967, 850, 712 $cm^{-1}$.

LC-MS (ESI) m/z $(M+Na)^+$ calcd for $C_{25}H_{33}BO_4Na$: 431.2, found: 431.2.

$[\alpha]^{23}_D$ = +12 (*c* = 1.0, $CHCl_3$); 84% ee, from (*R*,*S*)-**L1**.




**2-(6-Chloro-1-phenylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 9).** The title compound was synthesized according to **GP-2** from (1,6-dichlorohexyl)benzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 189 mg, 84% yield, 86% ee; (*S*,*R*)-**L1**: 182 mg, 80% yield, 87% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 10.6 min (major), 11.2 min (minor).

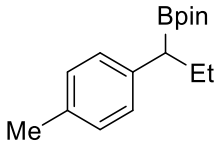
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.32 (t, *J* = 7.9 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.81 – 1.73 (m, 2H), 1.73 – 1.63 (m, 1H), 1.53 – 1.41 (m, 2H), 1.35 – 1.28 (m, 2H), 1.23 (s, 6H), 1.21 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.2, 128.3, 128.2, 125.2, 83.3, 45.1, 32.5, 32.4, 28.4, 26.8, 24.7, 24.6.

FT-IR (film): 2978, 1452, 1371, 1323, 1143, 967, 850, 701 $cm^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{18}H_{29}BClO_2$: 323.2, found: 323.2.

$[\alpha]^{23}_D$ = +13 (*c* = 1.0, $CHCl_3$); 86% ee, from (*R*,*S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-(*p*-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, Entry 10).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)-4-methylbenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 120 mg, 66% yield, 82% ee; (*S*,*R*)-**L1**: 112 mg, 61% yield, 82% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 8.4 min (minor), 9.4 min (major).

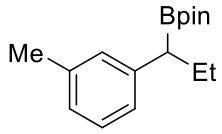
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.03 (m, 4H), 2.33 (s, 3H), 2.21 (t, *J* = 7.9 Hz, 1H), 1.95 – 1.82 (m, 1H), 1.74 – 1.61 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 0.93 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.2, 134.4, 128.9, 128.3, 83.1, 26.0, 24.7, 24.6, 21.0, 13.9.

FT-IR (film): 2978, 1462, 1360, 1322, 1144, 969, 852, 815 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{16}H_{25}BO_2$: 260.2, found: 260.1.

$[\alpha]^{23}_D$ = +17 (*c* = 1.0, $CHCl_3$); 82% ee, from (*R*,*S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-(*m*-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, Entry 11).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)-3-methylbenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 144 mg, 79% yield, 81% ee; (*S*,*R*)-**L1**: 136 mg, 75% yield, 82% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 7.3 min (minor), 8.6 min (major).

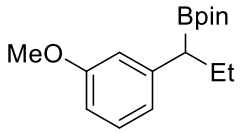
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 1H), 7.10 – 7.00 (m, 2H), 7.00 – 6.92 (m, 1H), 2.34 (s, 3H), 2.21 (t, *J* = 7.9 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.74 – 1.66 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 0.94 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 143.2, 137.6, 129.3, 128.1, 125.9, 125.3, 83.2, 25.9, 24.7, 24.6, 21.5, 14.0.

FT-IR (film): 2977, 1462, 1360, 1322, 1265, 1144, 968, 860, 708 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{16}H_{25}BO_2$: 260.2, found: 260.1.

$[\alpha]^{23}_D$ = +19 (*c* = 1.0, $CHCl_3$); 81% ee, from (*R*,*S*)-**L1**.




**2-(1-(3-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 12).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)-3-methoxybenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R*,*S*)-**L1**: 137 mg, 71% yield, 82% ee; (*S*,*R*)-**L1**: 130 mg, 67% yield, 80% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 15.3 min (minor), 16.4 min (major).

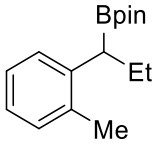
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.79 (m, 2H), 6.71 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.81 (s, 3H), 2.22 (t, *J* = 7.9 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.76 – 1.64 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 0.93 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.5, 145.0, 129.1, 120.9, 113.9, 110.6, 83.2, 55.1, 25.8, 24.7, 24.6, 13.9.

FT-IR (film): 2977, 1599, 1487, 1360, 1322, 1260, 1143, 1049, 860, 706 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{16}H_{25}BO_3$: 276.2, found: 276.1.

$[\alpha]^{23}_D$ = +10 (*c* = 1.0, $CHCl_3$); 82% ee, from (*R*,*S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-(*o*-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, Entry 13).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)-2-methylbenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 163 mg, 89% yield, 86% ee; (*S,R*)-**L1**: 160 mg, 88% yield, 86% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.4 min (minor), 9.5 min (major).

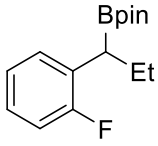
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.10 – 7.01 (m, 1H), 2.53 – 2.41 (m, 1H), 2.35 (s, 3H), 1.99 – 1.85 (m, 1H), 1.74 – 1.62 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 0.96 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.8, 136.0, 130.0, 127.7, 125.9, 124.9, 83.2, 25.3, 24.7, 24.6, 20.2, 14.1.

FT-IR (film): 2977, 1463, 1371, 1322, 1144, 968, 850, 729 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{16}H_{25}BO_2$: 260.2, found: 260.1.

$[\alpha]^{23}_D$ = +14 (*c* = 1.0, $CHCl_3$); 86% ee, from (*R,S*)-**L1**.




**2-(1-(2-Fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 14).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)-2-fluorobenzene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 159 mg, 86% yield, 82% ee; (*S,R*)-**L1**: 155 mg, 84% yield, 80% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 7.7 min (minor), 8.1 min (major).

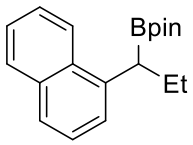
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.17 – 7.11 (m, 1H), 7.09 – 7.04 (m, 1H), 7.04 – 6.97 (m, 1H), 2.46 (t, *J* = 7.7 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.73 – 1.62 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 242 Hz), 130.5 (d, *J* = 3 Hz), 130.4 (d, *J* = 4 Hz), 126.7 (d, *J* = 8 Hz), 123.8 (d, *J* = 3 Hz), 115.0 (d, *J* = 33 Hz), 83.4, 24.7, 24.6, 24.5, 13.7.

FT-IR (film): 2978, 1490, 1362, 1325, 1144, 969, 851, 755 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{15}H_{22}BFO_2$: 264.2, found: 264.1.

$[\alpha]^{23}_D$ = +17 (*c* = 1.0, $CHCl_3$); 82% ee, from (*R,S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (Table 2, Entry 15).** The title compound was synthesized according to **GP-2** from 1-(1-chloropropyl)naphthalene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 189 mg, 91% yield, 84% ee; (*S,R*)-**L1**: 185 mg, 89% yield, 83% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 11.7 min (major), 12.9 min (minor).

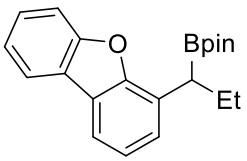
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.17 (m, 1H), 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71 (ddd, *J* = 6.2, 3.3, 0.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.39 (m, 2H), 3.09 – 2.93 (m, 1H), 2.18 – 2.04 (m, 1H), 1.97 – 1.84 (m, 1H), 1.26 (s, 6H), 1.22 (s, 6H), 1.04 (t, *J* = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 139.9, 134.0, 132.3, 128.7, 125.8, 125.7, 125.3, 125.24, 125.20, 124.2, 83.4, 25.3, 24.8, 24.6, 14.3.

FT-IR (film): 2977, 1462, 1379, 1320, 1264, 1143, 967, 778 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{19}H_{25}BO_2$: 296.2, found: 296.1.

$[\alpha]^{23}_D$ = +39 (*c* = 1.0, $CHCl_3$); 84% ee, from (*R,S*)-**L1**.




**2-(1-(Dibenzo[*b,d*]furan-4-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, Entry 16).** The title compound was synthesized according to **GP-2** from 4-(1-chloropropyl)dibenzo[*b,d*]furan and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 205 mg, 87% yield, 51% ee; (*S,R*)-**L1**: 198 mg, 84% yield, 51% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 8.1 min (minor), 10.9 min (major).

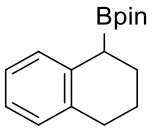
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.97 (ddd, $J$ = 7.6, 1.4, 0.7 Hz, 1H), 7.79 (dd, $J$ = 7.5, 1.4 Hz, 1H), 7.59 (dt, $J$ = 8.3, 1.0 Hz, 1H), 7.46 (ddd, $J$ = 8.3, 7.3, 1.3 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 2.84 (t, $J$ = 7.8 Hz, 1H), 2.15 – 2.00 (m, 1H), 1.99 – 1.83 (m, 1H), 1.29 (s, 6H), 1.25 (s, 6H), 1.00 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 155.9, 154.8, 127.7, 127.2, 126.7, 124.9, 123.6, 122.8, 122.4, 120.6, 117.6, 111.6, 83.4, 24.7, 24.6, 24.5, 14.0.

FT-IR (film): 2976, 2870, 1451, 1378, 1187, 1143, 968, 846, 752 cm$^{-1}$.

GC-MS (EI) m/z $(M+H)^+$ calcd for $C_{21}H_{26}BO_3$: 337.2, found: 337.2.

$[\alpha]^{24}_D$ = +25 ($c$ = 1.0, $CHCl_3$); 51% ee, from (*R,S*)-**L1**.




**4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (Table 2, Entry 17).** The title compound was synthesized according to **GP-2** from 1-chloro-1,2,3,4-tetrahydronaphthalene and $B_2pin_2$, and it was purified by column chromatography on silica gel (5% $Et_2O$ in hexanes). Colorless oil.

(*R,S*)-**L1**: 143 mg, 79% yield, 81% ee; (*S,R*)-**L1**: 150 mg, 83% yield, 81% ee.

HPLC analysis: After oxidation (**GP-3**), the ee was determined on a CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R,S*)-**L1**: 9.1 min (major), 9.9 min (minor).

$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.18 – 7.13 (m, 1H), 7.12 – 7.03 (m, 3H), 2.80 (td, $J$ = 6.0, 2.5 Hz, 2H), 2.62 (t, $J$ = 6.4 Hz, 1H), 1.99 – 1.87 (m, 3H), 1.84 – 1.72 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 137.6, 136.6, 129.4, 129.3, 125.3, 124.8, 83.3, 29.8, 25.1, 24.7, 24.6, 22.7.

FT-IR (film): 2977, 1449, 1379, 1327, 1144, 970, 854, 737 cm$^{-1}$.

LC-MS (ESI) m/z $(M+H)^+$ calcd for $C_{16}H_{24}BO_2$: 259.2, found: 259.2.

$[\alpha]^{23}_D$ = +10 ($c$ = 1.0, $CHCl_3$); 81% ee, from (*R,S*)-**L1**.

## IV. Effect of Reaction Parameters

**General Procedure 4 (GP-4): Effect of reaction parameters.** This procedure was carried out in a nitrogen-filled glove box.

**Preparation of the catalyst.** An oven-dried 4 mL vial that contained a magnetic stir bar was charged with $NiCl_2$·glyme (4.4 mg, 0.020 mmol, 10 mol%), **L1** (9.4 mg, 0.024 mmol, 12 mol%), and DME (1.0 mL). The vial was capped with a PTFE-lined septum cap, and the reaction mixture was stirred at room temperature for 1 h.

**Preparation of a solution of the nucleophile.** An oven-dried 4 mL vial that contained a magnetic stir bar was charged in turn with *t*-BuOK (31 mg, 0.28 mmol, 1.4 equiv), CPME (0.60 mL), and 2-phenylethanol (36 μL, 0.30 mmol, 1.5 equiv). The resulting suspension was stirred at room temperature for 3 min, and then $B_2pin_2$ (71 mg, 0.28 mmol, 1.4 equiv) was added. The vial was then capped, and the resulting suspension was stirred at room temperature for 40 min.

**Enantioconvergent borylation.** The benzylic chloride (0.20 mmol, 1.0 equiv) was added via syringe to the suspension of the catalyst. The resulting mixture was stirred for 5 min, and then the solution of the nucleophile was added via syringe over ~1 min. Then, the vial was capped and removed from the glove box. The reaction mixture was stirred at room temperature for 3 h.

**Workup.** *n*-Dodecane (46 μL, 0.20 mmol) was added to the reaction mixture via syringe. Then, the reaction mixture was filtered through a short pad of silica gel, eluting with $Et_2O$ (5.0 mL). The yield was determined via GC analysis.

**Determination of enantioselectivity.** The filtered reaction mixture was concentrated, and then the residue was dissolved in THF/$H_2O$ (1:1; 4.0 mL). Next, $NaBO_3$·$4H_2O$ (~150 mg) was added, and the resulting mixture was stirred vigorously at room temperature for 4 h. Then, the mixture was extracted with $Et_2O$ (4.0 mL). The resulting organic phase was dried over anhydrous $Na_2SO_4$ and concentrated, and the residue was purified by preparative thin-layer chromatography. The ee of the benzylic alcohol was determined via HPLC analysis.

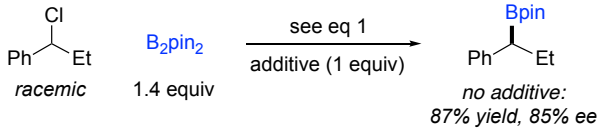
(1-Chloropropyl)benzene was reacted with $B_2pin_2$ according to **GP-4**. The yields were determined via GC analysis, using *n*-dodecane as an internal standard. The ee's were determined via HPLC analysis, after stereospecific oxidation of the reaction mixture and purification by preparative thin-layer chromatography. All data are the average of two experiments. A negative value for ee signifies that the major product is the R enantiomer.

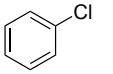
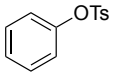
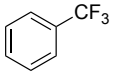
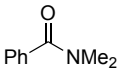
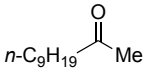
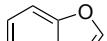
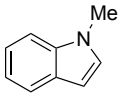
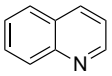
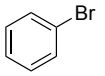
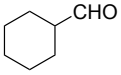
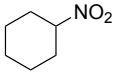
## V. Effect of Additives

(1-Chloropropyl)benzene was reacted with $B_2pin_2$ according to **GP-4**, in the presence of 1.0 equiv of each of the additives shown below. The additive was added after the addition of (1-chloropropyl)benzene.

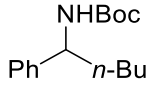
The yields were determined via GC analysis, using *n*-dodecane as an internal standard. The ee's were determined via HPLC analysis, after stereospecific oxidation of the reaction mixture and purification by preparative thin-layer chromatography. All data are the average of two experiments.

**Table S–1.**




| entry | additive | recovery of additive (%) | yield (%) | ee (%) |
|---|---|---|---|---|
| 1 | none | – | 87 | 85 |
| 2 |  | >95 | 88 | 83 |
| 3 |  | 90 | 87 | 84 |
| 4 |  | >95 | 88 | 84 |
| 5 |  | >95 | 88 | 84 |
| 6 |  | 92 | 82 | 83 |
| 7 |  | 90 | 88 | 84 |
| 8 |  | >95 | 88 | 84 |
| 9 |  | >95 | 81 | 84 |
| 10 |  | >95 | 84 | 84 |
| 11 |  | >95 | 86 | 83 |
| 12 |  | >95 | 73 | 83 |
| 13 |  | 92 | 45 | 75 |
| 14 |  | >95 | 25 | 74 |
| 15 |  | 83 | 32 | 66 |
| 16 |  | 24 | <2 | – |

## VI. Derivatization of the Borylation Products




***tert*-Butyl (1-phenylpentyl)carbamate (Figure 3).**[4] An oven-dried 25 mL flask equipped with a magnetic stir bar and a septum was evacuated and backfilled with $N_2$ (3 cycles). A solution of *O*-methylhydroxylamine (2.8 M in THF; 0.43 mL, 1.2 mmol, 3.0 equiv) was added, followed by anhydrous THF (4.0 mL). The reaction flask was cooled to –78 °C in a dry-ice/acetone bath. A solution of *n*-BuLi (2.4 M in hexanes; 0.50 mL, 1.2 mmol, 3.0 equiv) was added dropwise via syringe over 1 min, and then the reaction mixture was stirred at –78 °C for 30 min. Next, a solution of 4,4,5,5-tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (110 mg, 0.40 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was added dropwise via syringe over 1 min to the solution of deprotonated *O*-methylhydroxylamine. The reaction flask was allowed to warm to room temperature, and then it was heated to 60 °C. After stirring at 60 °C for 12 h, the flask was allowed to cool to room temperature, and then $Boc_2O$ (0.29 mL, 1.3 mmol, 3.2 equiv) was added. After stirring at room temperature for 1 h, the reaction was quenched by the addition of water (8.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The residue was purified by column chromatography (5%→10% EtOAc in hexanes) to provide the desired product as a white solid.

(*R*,*S*)-**L1**: 81 mg, 77% yield, 88% ee; (*S*,*R*)-**L1**: 88 mg, 84% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 6.0 min (minor), 7.0 min (major).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.20 – 7.15 (m, 3H), 4.97 – 4.59 (m, 1H), 4.59 – 4.20 (m, 1H), 1.81 – 1.58 (m, 2H), 1.34 (s, 9H), 1.26 – 1.15 (m, 4H), 0.80 (t, *J* = 7.0 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.2, 143.2, 128.5, 127.0, 126.3, 79.3, 54.9, 36.8, 28.4, 28.3, 22.5, 14.0.

FT-IR (film): 3379, 2957, 1683, 1521, 1253, 1174, 1010, 703 $cm^{-1}$.

LC-MS (ESI) m/z $(M+Na)^+$ calcd for $C_{16}H_{25}NO_2Na$: 286.2, found: 286.2.

$[\alpha]^{23}_D$ = –28 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.

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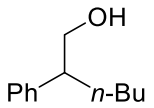
[4] S. N. Mlynarski, A. S. Karns, J. P. Morken, *J. Am. Chem. Soc.* **2012**, *134*, 16449–16451.




**2-Phenylhexan-1-ol (Figure 3).**[5] An oven-dried 25 mL flask equipped with a magnetic stir bar and a septum, was evacuated and backfilled with $N_2$ (3 cycles), and then 4,4,5,5-tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (110 mg, 0.40 mmol, 1.0 equiv), bromochloromethane (52 μL, 0.80 mmol, 2.0 equiv), and anhydrous $Et_2O$ (8.0 mL) were added via syringe sequentially. The reaction flask was cooled to –78 °C in a dry-ice/acetone bath. Then, a solution of *n*-BuLi in hexanes (2.4 M; 0.32 mL, 0.80 mmol, 2.0 equiv) was added dropwise via syringe over 1 min. The reaction mixture was allowed to slowly warm to room temperature and then stirred for 2 h. Next, the reaction was quenched by the addition of a saturated aqueous solution of $NH_4Cl$ (5.0 mL), and the mixture was extracted with $Et_2O$ (3 x 10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was then dissolved in $Et_2O$ (6.0 mL). MeOH (1.0 mL), aqueous NaOH (2 N; 2.0 mL), and then aqueous $H_2O_2$ (30 weight% in $H_2O$; 0.20 mL) were added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Next, the layers were separated, and the aqueous layer was extracted with $Et_2O$ (3 x 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (10% EtOAc in hexanes), which furnished the desired product as a colorless oil.

(*R*,*S*)-**L1**: 61 mg, 86% yield, 88% ee; (*S*,*R*)-**L1**: 63 mg, 88% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALCEL AD-H column (1% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 10.4 min (minor), 11.0 min (major).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.18 – 7.12 (m, 3H), 3.71 – 3.58 (m, 2H), 2.78 – 2.60 (m, 1H), 1.68 – 1.57 (m, 1H), 1.55 – 1.44 (m, 1H), 1.25 – 1.16 (m, 2H), 1.15 – 1.02 (m, 2H), 0.77 (t, *J* = 7.1 Hz, 3H).

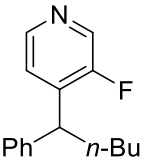
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.6, 128.1, 126.7, 67.7, 48.7, 31.8, 29.6, 22.8, 14.0.

FT-IR (film): 3349, 2929, 1494, 1453, 1054, 1017, 758, 699 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{12}H_{18}O$: 178.1, found: 178.1.

$[\alpha]^{23}_D$ = +14 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.

[5] A. Chen, L. Ren, C. M. Crudden, *J. Org. Chem.* **1999**, *64*, 9704–9710.




**3-Fluoro-4-(1-phenylpentyl)pyridine (Figure 3).**[6] An oven-dried 25 mL flask equipped with a magnetic stir bar and a septum was evacuated and backfilled with $N_2$ (3 cycles). Diisopropylamine (112 μL, 0.80 mmol, 2.0 equiv) and anhydrous THF (2.0 mL) were added sequentially. The reaction flask was cooled to –60 °C. A solution of *n*-BuLi in hexanes (2.4 M; 0.37 mL, 0.88 mmol, 2.2 equiv) was added dropwise via syringe over 1 min, and the resulting mixture was stirred at –60 °C for 30 min. Then, a solution of 3-fluoropyridine (69 μL, 0.80 mmol, 2.0 equiv) in anhydrous THF (1.0 mL) was added dropwise via syringe over 1 min, and the resulting mixture was stirred at –60 °C for 30 min. Next, the mixture was cooled to –78 °C, and a solution of 4,4,5,5-tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (110 mg, 0.40 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was added dropwise via syringe over 1 min. The reaction mixture was stirred at –78 °C for 2 h, and then 2,2,2-trichlorethoxycarbonyl chloride (220 μL, 1.6 mmol, 4.0 equiv) was added. The resulting mixture was stirred at –78 °C for 8 h and then allowed to warm to room temperature overnight. Next, the mixture was diluted with $Et_2O$ (10 mL) and $H_2O$ (5.0 mL), the layers were separated, and the aqueous layer was neutralized with saturated aqueous $NaHCO_3$ (5.0 mL). The aqueous layer was extracted with $Et_2O$ (2 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was dissolved in THF (2.0 mL) and cooled to 0 °C. Aqueous NaOH (2 M; 1.6 mL) and aqueous $H_2O_2$ (30 weight% in $H_2O$; 1.6 mL) were added sequentially, and the mixture was stirred at room temperature for 12 h. $Et_2O$ (10 mL) was then added, and the layers were separated. The aqueous layer was acidified with aqueous HCl (1 M; 5.0 mL) and extracted with $Et_2O$ (2 x 10 mL). The aqueous layer was then neutralized with saturated aqueous $NaHCO_3$ (10 mL) and extracted with $Et_2O$ (2 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (10%→20% EtOAc in hexanes), which provided the desired product as a pale-yellow oil.

(*R*,*S*)-**L1**: 68 mg, 70% yield, 88% ee; (*S*,*R*)-**L1**: 72 mg, 74% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 5.6 min (major), 6.7 min (minor).

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.19 – 7.12 (m, 4H), 4.18 (t, *J* = 7.8 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.31 – 1.24 (m, 2H), 1.22 – 1.15 (m, 2H), 0.80 (t, *J* = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.9 (d, *J* = 252 Hz), 145.8 (d, *J* = 5 Hz), 142.1, 140.8 (d, *J* = 12 Hz), 138.0 (d, *J* = 25 Hz), 128.7, 127.9, 126.8, 122.9 (d, *J* = 2 Hz), 43.1 (d, *J* = 1 Hz), 33.9, 29.9, 22.5, 13.9.

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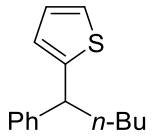
[6] J. Llaveria, D. Leonori, V. K. Aggarwal, *J. Am. Chem. Soc.* **2015**, *137*, 10958–10961.

FT-IR (film): 3029, 2931, 1600, 1491, 1413, 1243, 839, 699 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{16}H_{18}FN$: 243.1, found: 243.1.

$[\alpha]^{23}_D$ = –3.9 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.




**2-(1-Phenylpentyl)thiophene (Figure 3).**[7] An oven-dried 25 mL flask equipped with a magnetic stir bar and a septum was evacuated and backfilled with $N_2$ (3 cycles), and then thiophene (45 μL, 0.56 mmol, 1.4 equiv) and anhydrous THF (2.0 mL) were added sequentially. The reaction flask was cooled to –78 °C in a dry-ice/acetone bath, and then a solution of *n*-BuLi in hexanes (2.4 M; 0.23 mL, 0.56 mmol, 1.4 equiv) was added dropwise by syringe over 1 min. Next, the reaction mixture was allowed to warm to 0 °C and stirred for 30 min. The mixture was then cooled to –78 °C, and a solution of 4,4,5,5-tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (110 mg, 0.40 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was added dropwise via syringe over 1 min. The resulting mixture was stirred at –78 °C for 1 h, and then a solution of *N*-bromosuccinimide (100 mg, 0.56 mmol, 1.4 equiv) in anhydrous THF (1.0 mL) was added dropwise. After 1 h at –78 °C, saturated aqueous $Na_2SO_3$ (2.0 mL) was added, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with EtOAc (10 mL) and water (5.0 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (15% $CH_2Cl_2$ in hexanes), which provided the desired product as a colorless oil.

(*R*,*S*)-**L1**: 78 mg, 85% yield, 88% ee; (*S*,*R*)-**L1**: 75 mg, 81% yield, 88% ee.

HPLC analysis: The ee was determined on a CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min); retention times for compound obtained using (*R*,*S*)-**L1**: 10.6 min (minor), 12.4 min (major).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.85 (dt, *J* = 3.5, 1.1 Hz, 1H), 4.24 – 4.04 (m, 1H), 2.23 – 1.98 (m, 2H), 1.45 – 1.24 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.9, 144.8, 128.5, 127.7, 126.50, 126.46, 123.6, 123.3, 46.9, 37.2, 30.1, 22.6, 14.0.

FT-IR (film): 3027, 2929, 1494, 1453, 696 $cm^{-1}$.

GC-MS (EI) m/z $(M)^+$ calcd for $C_{15}H_{18}S$: 230.1, found: 230.0.

$[\alpha]^{23}_D$ = +19 (*c* = 1.0, $CHCl_3$); 88% ee, from (*R*,*S*)-**L1**.

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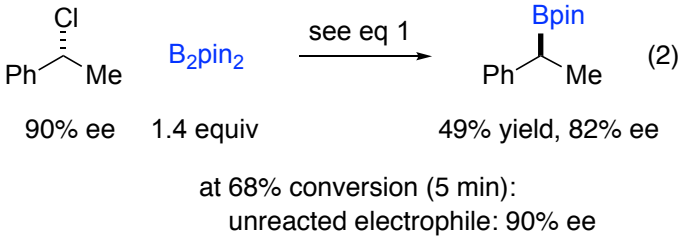
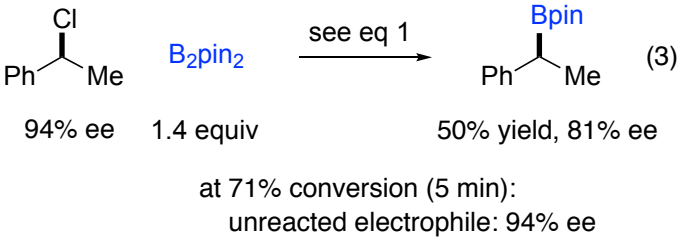
[7] A. Bonet, M. Odachowski, D. Leonori, S. Essafi, V. K. Aggarwal, *Nat. Chem.* **2014**, *6*, 584–589.

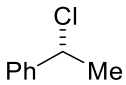
## VII. Mechanistic Study

Enantioenriched (1-chloroethyl)benzene was obtained via HPLC resolution on a chiral OB-H column (pentane, 2.5 mL/min); retention times: 5.9 min ((*S*)-(1-chloroethyl)benzene, 94% ee), 6.7 min ((*R*)-(1-chloroethyl)benzene, 90% ee).

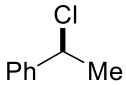



Enantioenriched (1-chloroethyl)benzene was reacted with $B_2pin_2$ according to **GP-4**. The conversion and the yield were determined via GC analysis, using *n*-dodecane as an internal standard. The ee of the product was determined via HPLC analysis, after stereospecific oxidation of the reaction mixture and purification by preparative thin-layer chromatography. The ee of (1-chloroethyl)benzene was determined via GC analysis.




**(*R*)-(1-Chloroethyl)benzene**. The ee was determined via GC analysis on a CHIRALDEX G-TA column (80 – 180 °C, ramp: 5 °C /min); retention times: 6.2 min (major), 6.4 (minor).




**(*S*)-(1-Chloroethyl)benzene**. The ee was determined via GC analysis on a CHIRALDEX G-TA column (80 – 180 °C, ramp: 5 °C /min); retention times: 6.2 min (minor), 6.4 (major).

## VIII. Assignment of Absolute Configuration

**(*S*)-1-Phenylethan-1-ol.** 4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane was prepared according **GP-2**, using (*R*,*S*)-**L1**. The boronate ester was stereospecifically oxidized as described in **GP-3** to give (*S*)-1-phenylethan-1-ol.

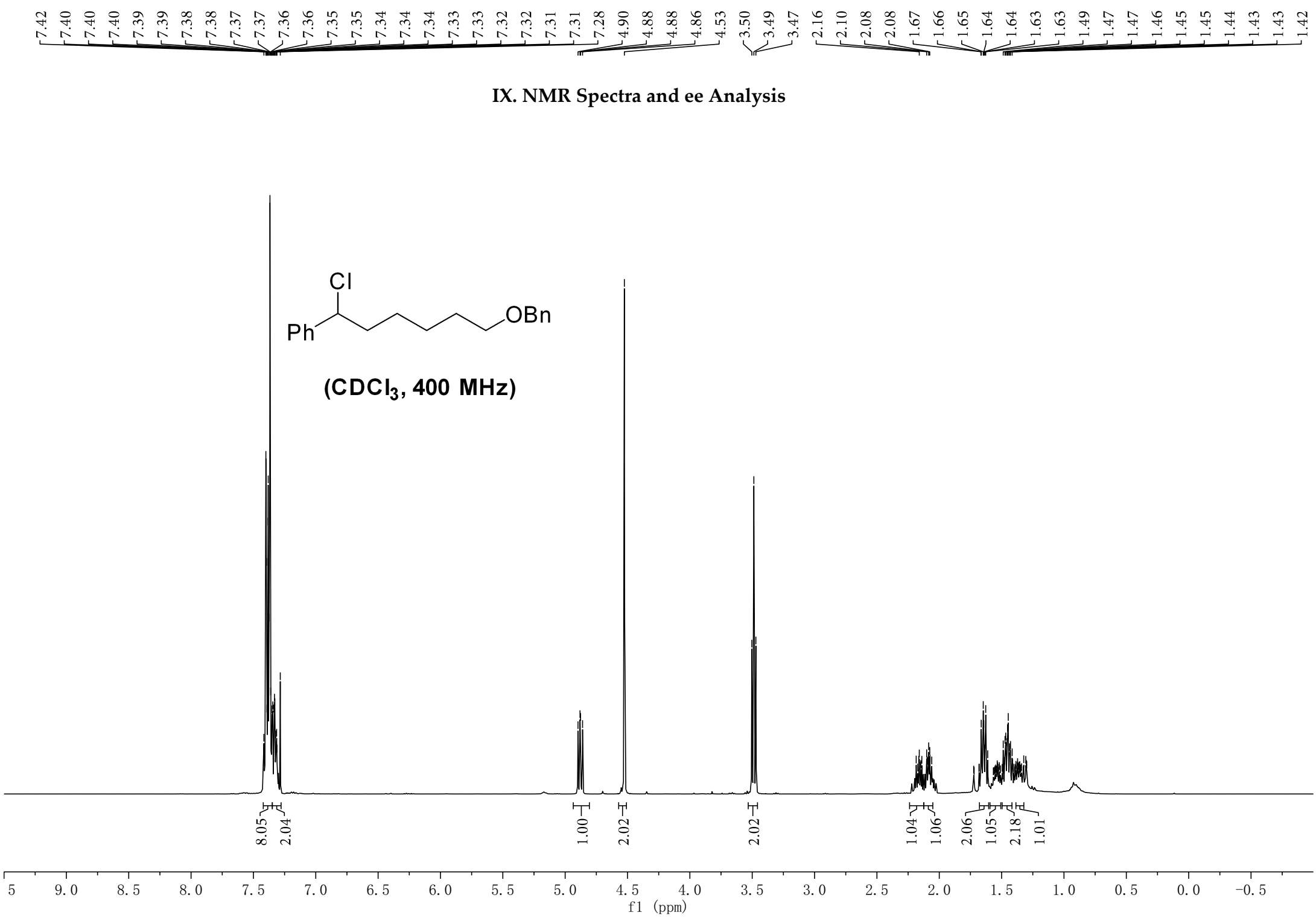
HPLC analysis: The ee was determined on a CHIRALCEL OD-H column (3% *i*-PrOH in hexanes, 1.0 mL/min): retention times: 11.7 min (minor), 14.8 min (major).

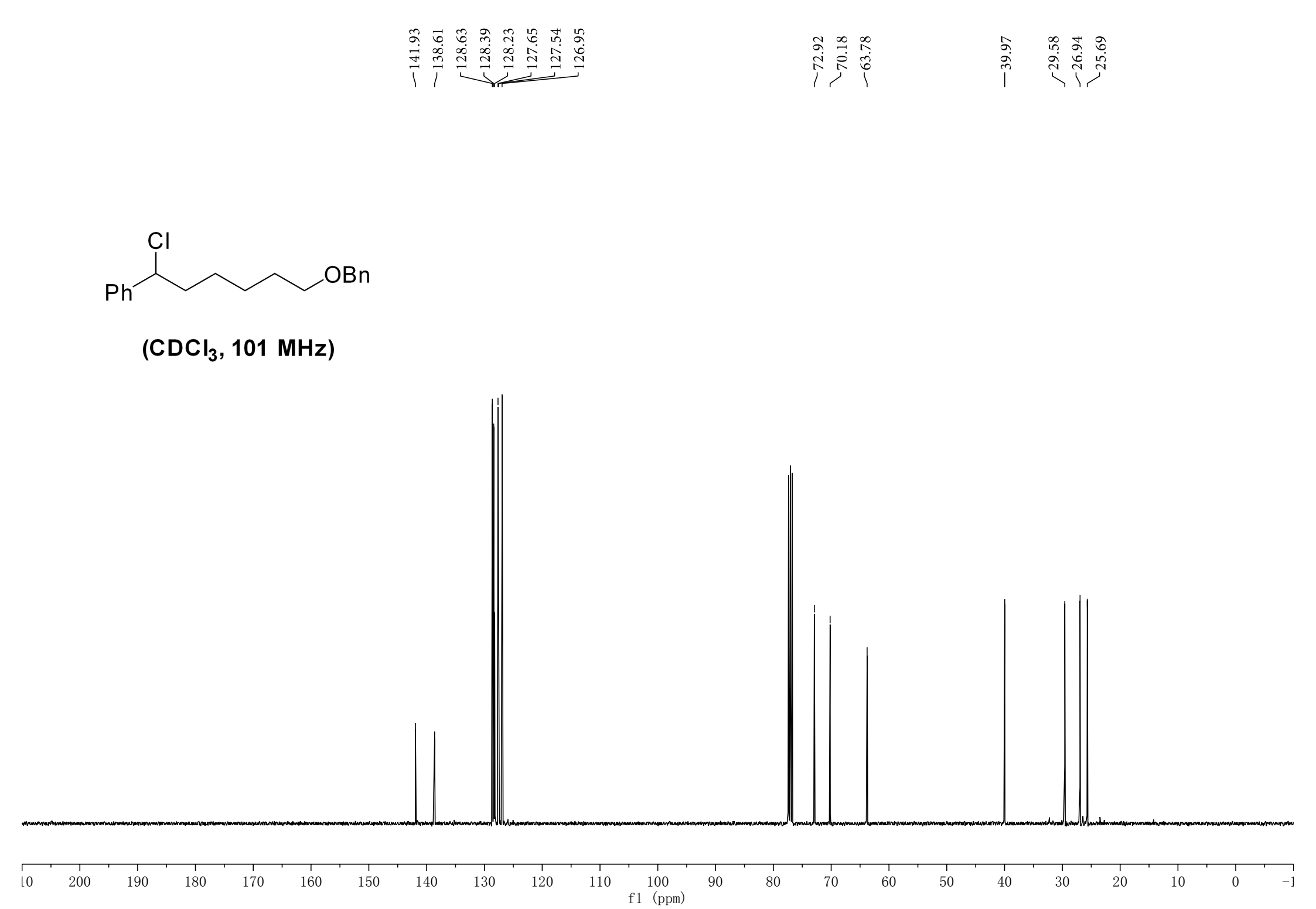
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 4H), 7.33 – 7.26 (m, 1H), 4.91 (qd, *J* = 6.5, 2.6 Hz, 1H), 2.14 (s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H).

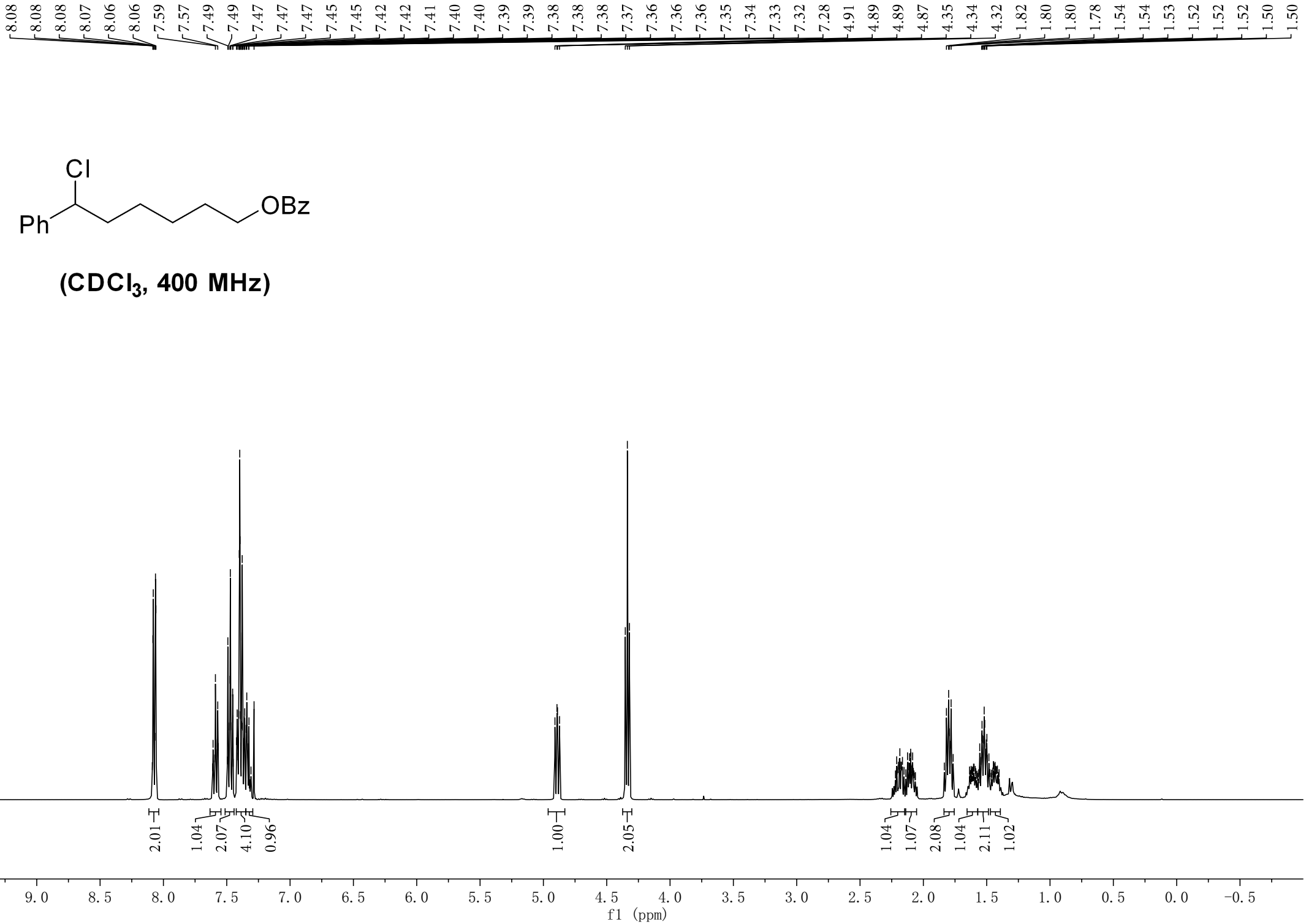
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.8, 128.5, 127.5, 125.4, 70.4, 25.2.

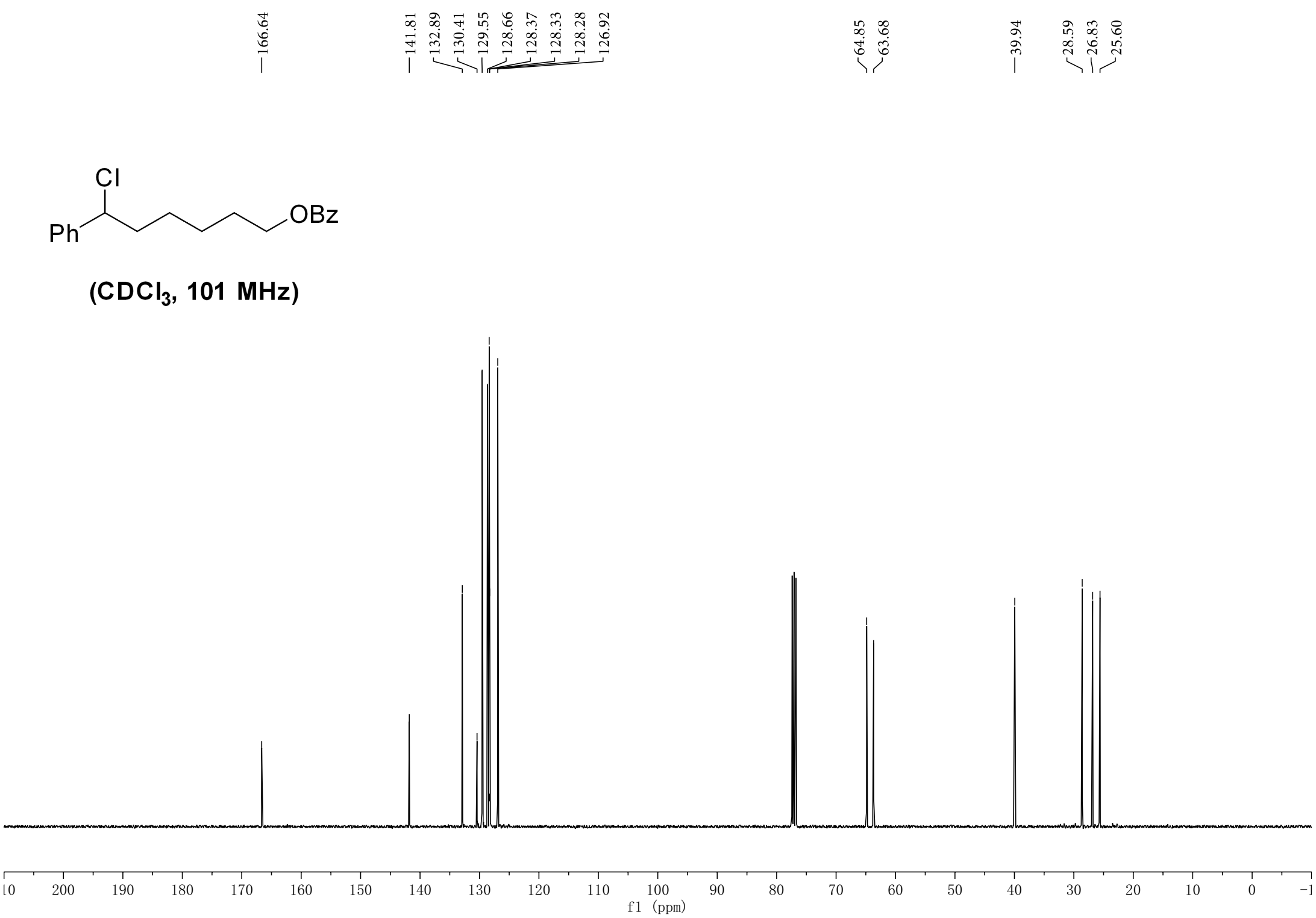
Determination of the absolute configuration: The absolute configuration was assigned by comparing the retention time to commercially available 1-phenylethan-1-ol, under the same conditions: (*R*)-1-phenylethan-1-ol [1517-69-7] 11.2 min (major); (*S*)-1-phenylethan-1-ol [1445-91-6] 14.4 min (major).

## IX. NMR Spectra and ee Analysis

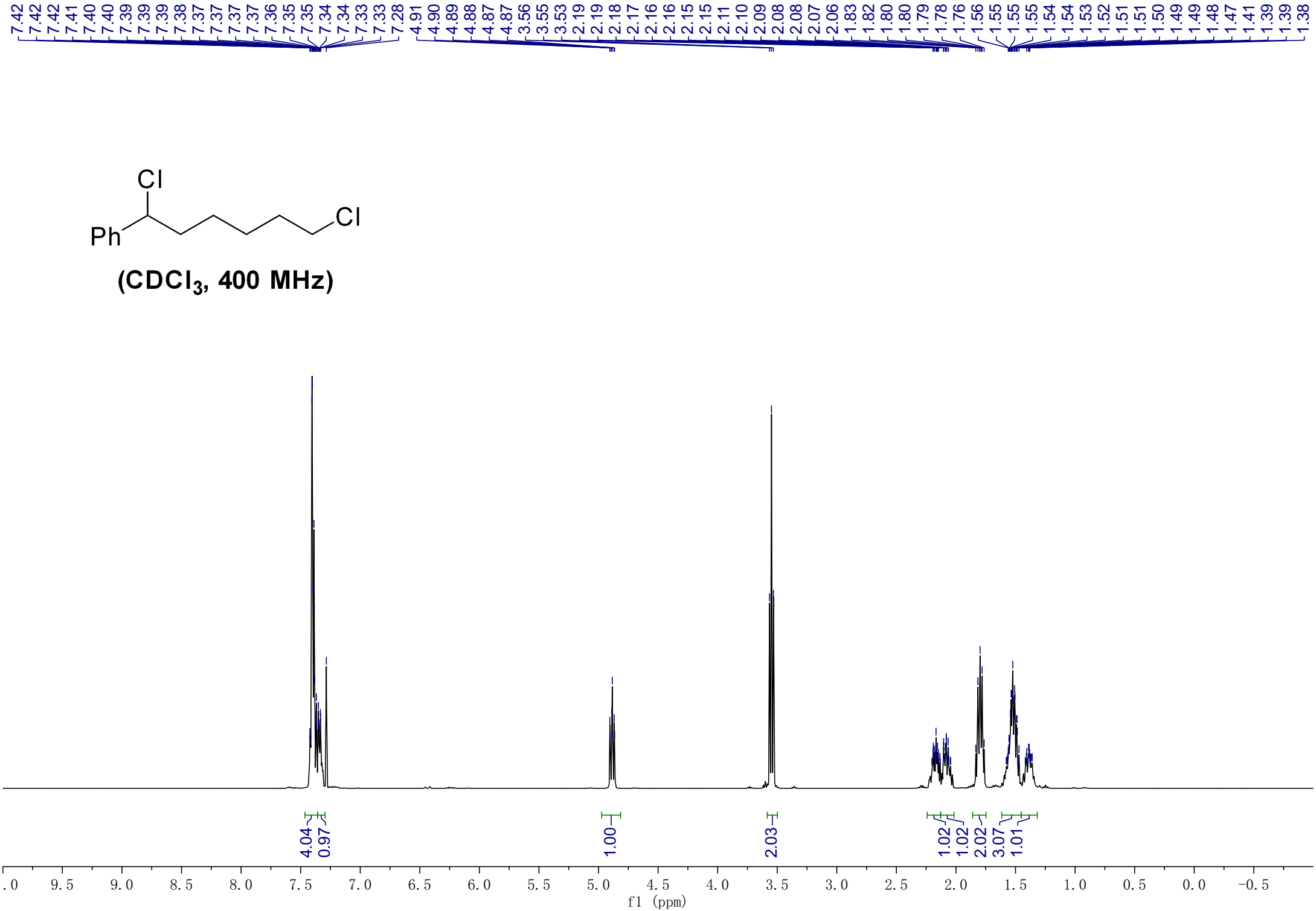


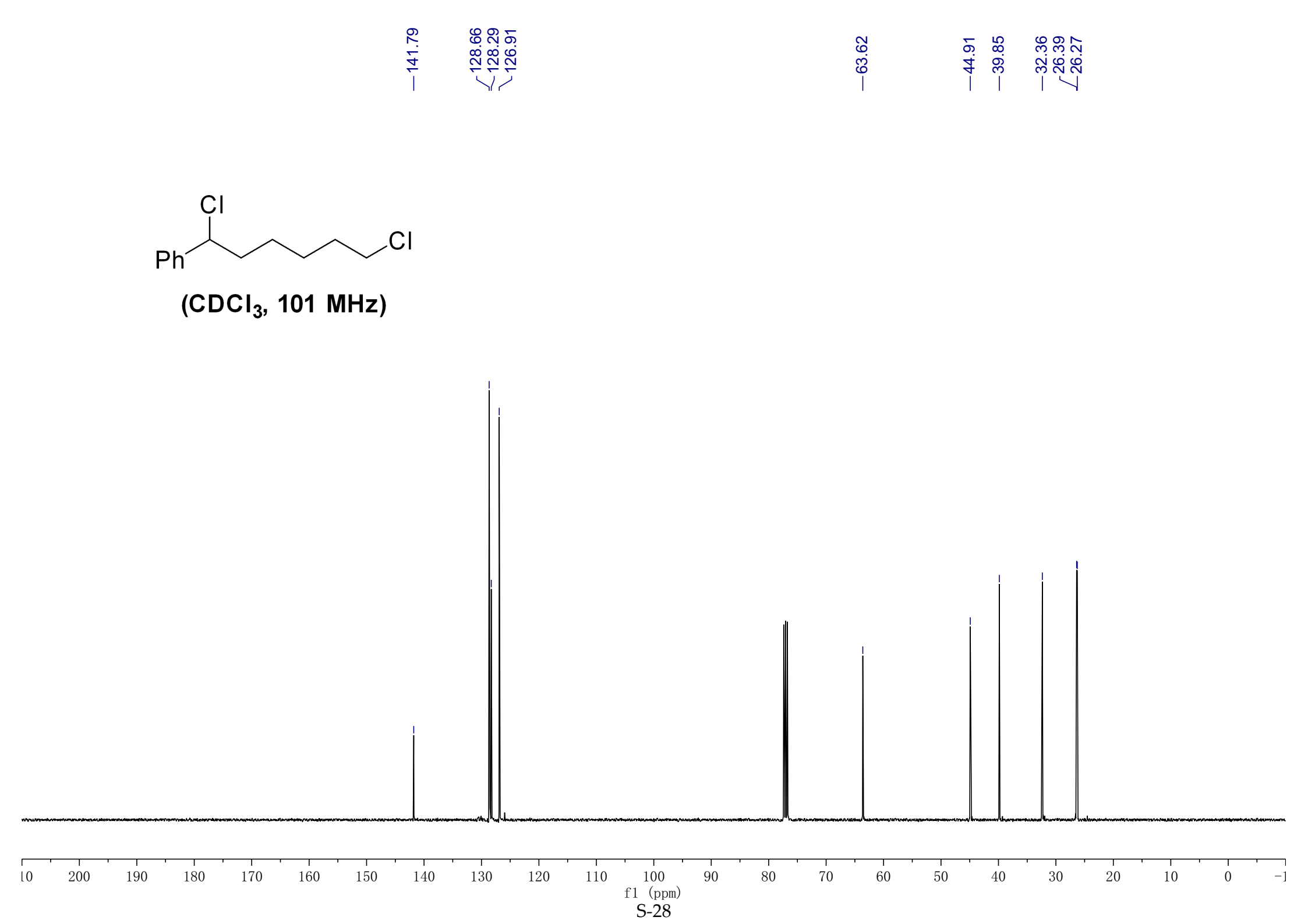

141.93
138.61
128.63
128.39
128.23
127.65
127.54
126.95
72.92
70.18
63.78
39.97
29.58
26.94
25.69
Cl
Ph
OBn
(CDCl3, 101 MHz)
f1 (ppm)

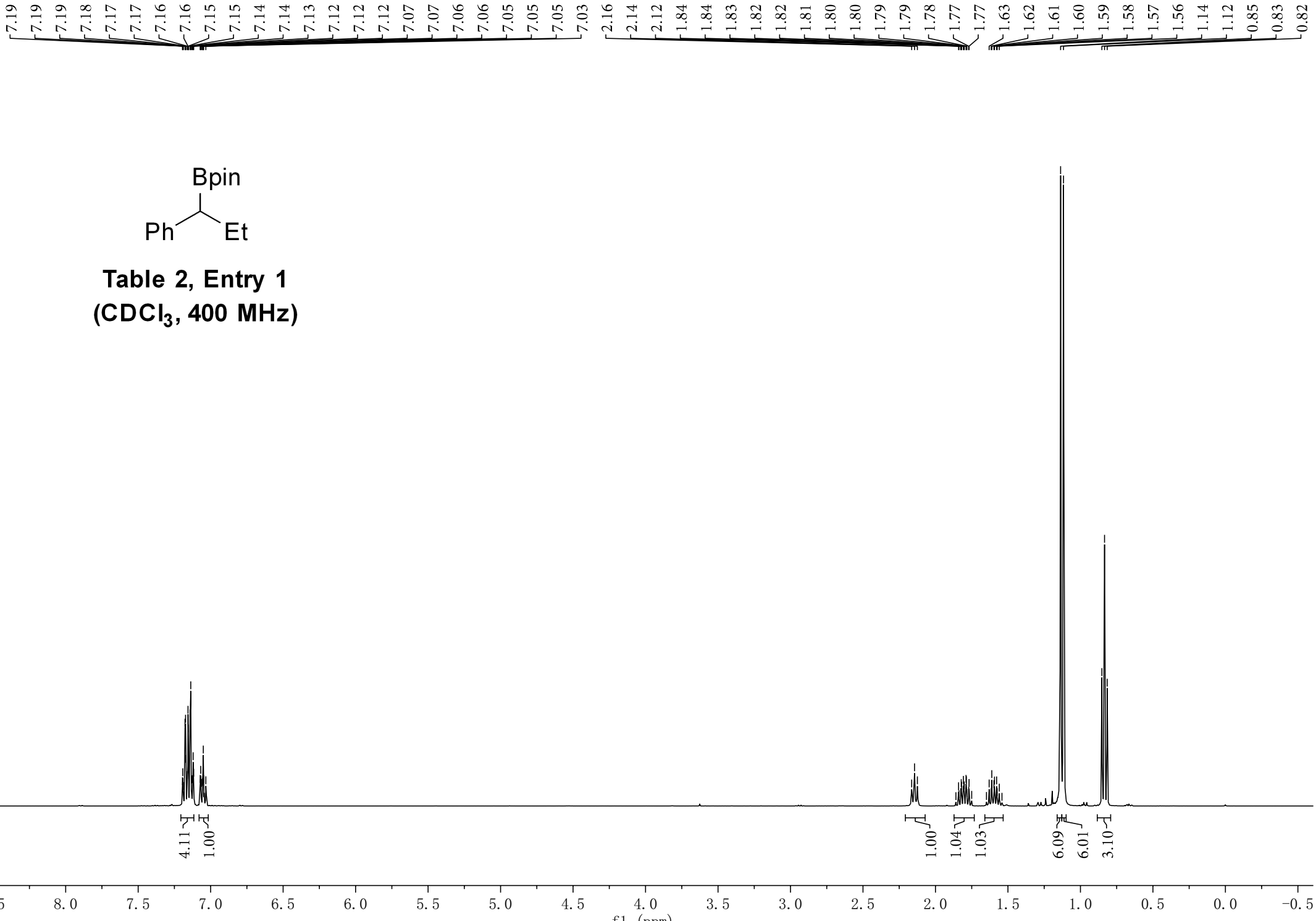

8.08 8.08 8.08 8.07 8.06 8.06 7.59 7.57 7.49 7.49 7.47 7.47 7.47 7.45 7.45 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.33 7.32 7.28 4.91 4.89 4.89 4.87 4.35 4.34 4.32 1.82 1.80 1.80 1.78 1.54 1.54 1.53 1.52 1.52 1.52 1.50 1.50
Cl
Ph
OBz
(CDCl3, 400 MHz)
2.01 1.04 2.07 4.10 0.96 1.00 2.05 1.04 1.07 2.08 1.04 2.11 1.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)




**($CDCl_3$, 101 MHz)**


7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.28
4.91 4.90 4.89 4.88 4.87 4.87 3.56 3.55 3.53 2.19 2.19 2.18 2.17 2.16 2.16 2.15 2.15 2.11 2.10 2.09 2.08 2.08 2.07 2.06 1.83 1.82 1.80 1.80 1.79 1.78 1.76 1.56 1.55 1.55 1.55 1.54 1.54 1.53 1.52 1.51 1.51 1.50 1.49 1.49 1.48 1.47 1.41 1.39 1.39 1.38
Cl
Ph
Cl
(CDCl3, 400 MHz)
4.04
0.97
1.00
2.03
1.02
1.02
2.02
3.07
1.01
f1 (ppm)


141.79
128.66
128.29
126.91
63.62
44.91
39.85
32.36
26.39
26.27
Cl
Ph
Cl
(CDCl3, 101 MHz)
f1 (ppm)


7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.12 7.12 7.07 7.07 7.06 7.06 7.05 7.05 7.05 7.03
2.16 2.14 2.12 1.84 1.84 1.83 1.82 1.82 1.81 1.80 1.80 1.79 1.79 1.78 1.77 1.77 1.63 1.62 1.61 1.60 1.59 1.58 1.57 1.56 1.14 1.12 0.85 0.83 0.82
Bpin
Ph
Et
Table 2, Entry 1
(CDCl3, 400 MHz)
4.11
1.00
1.00
1.04
1.03
6.09
6.01
3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

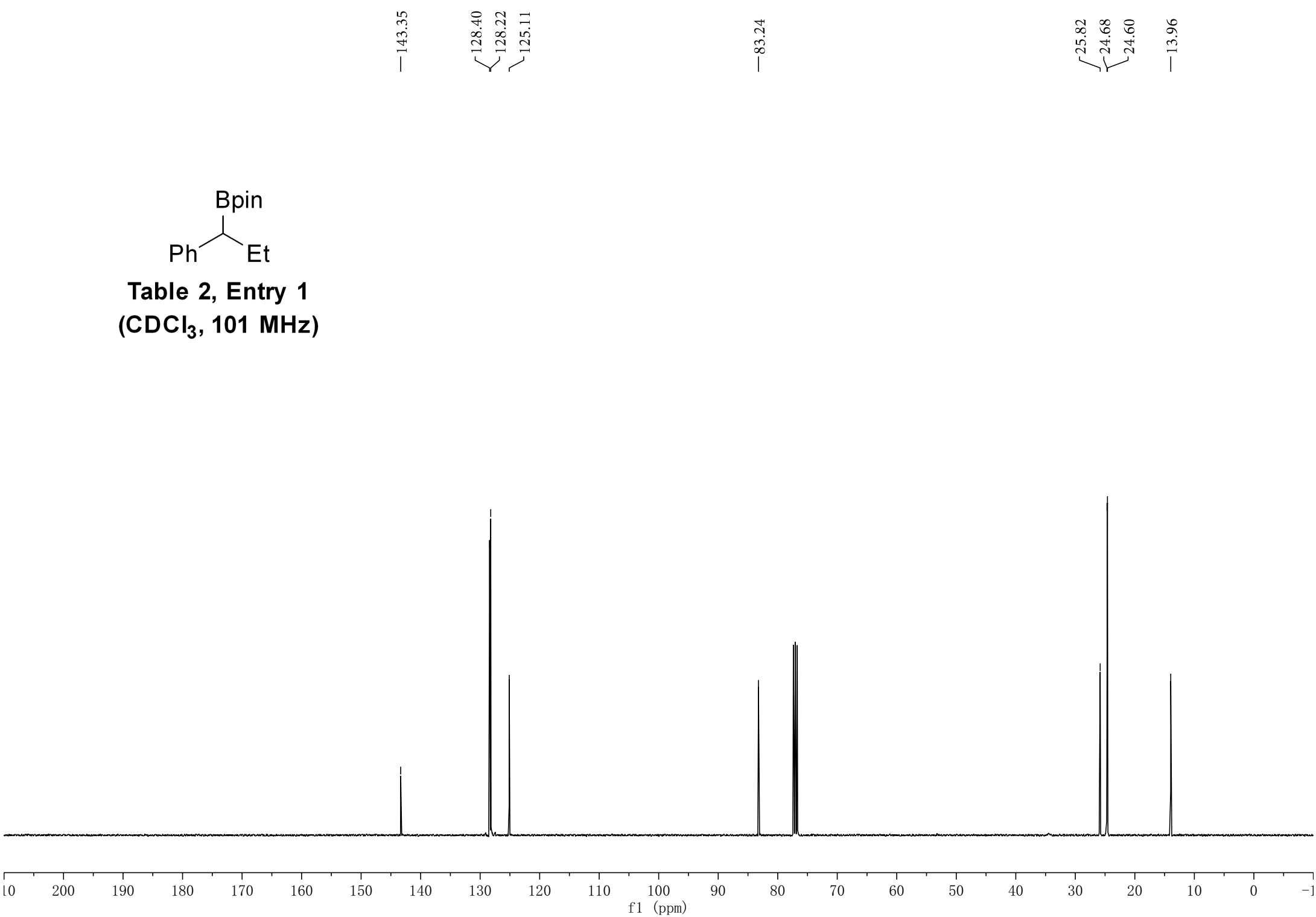
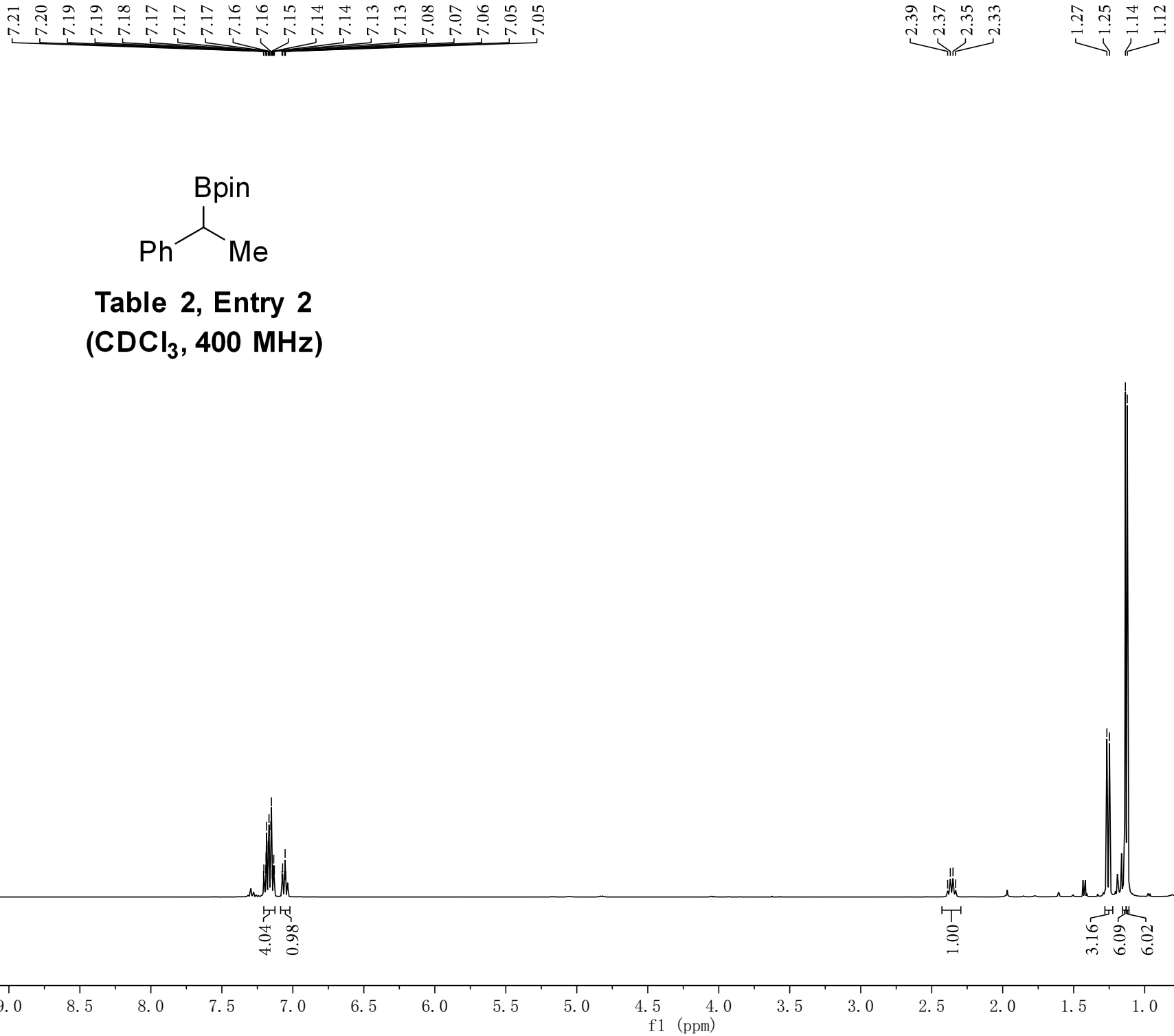
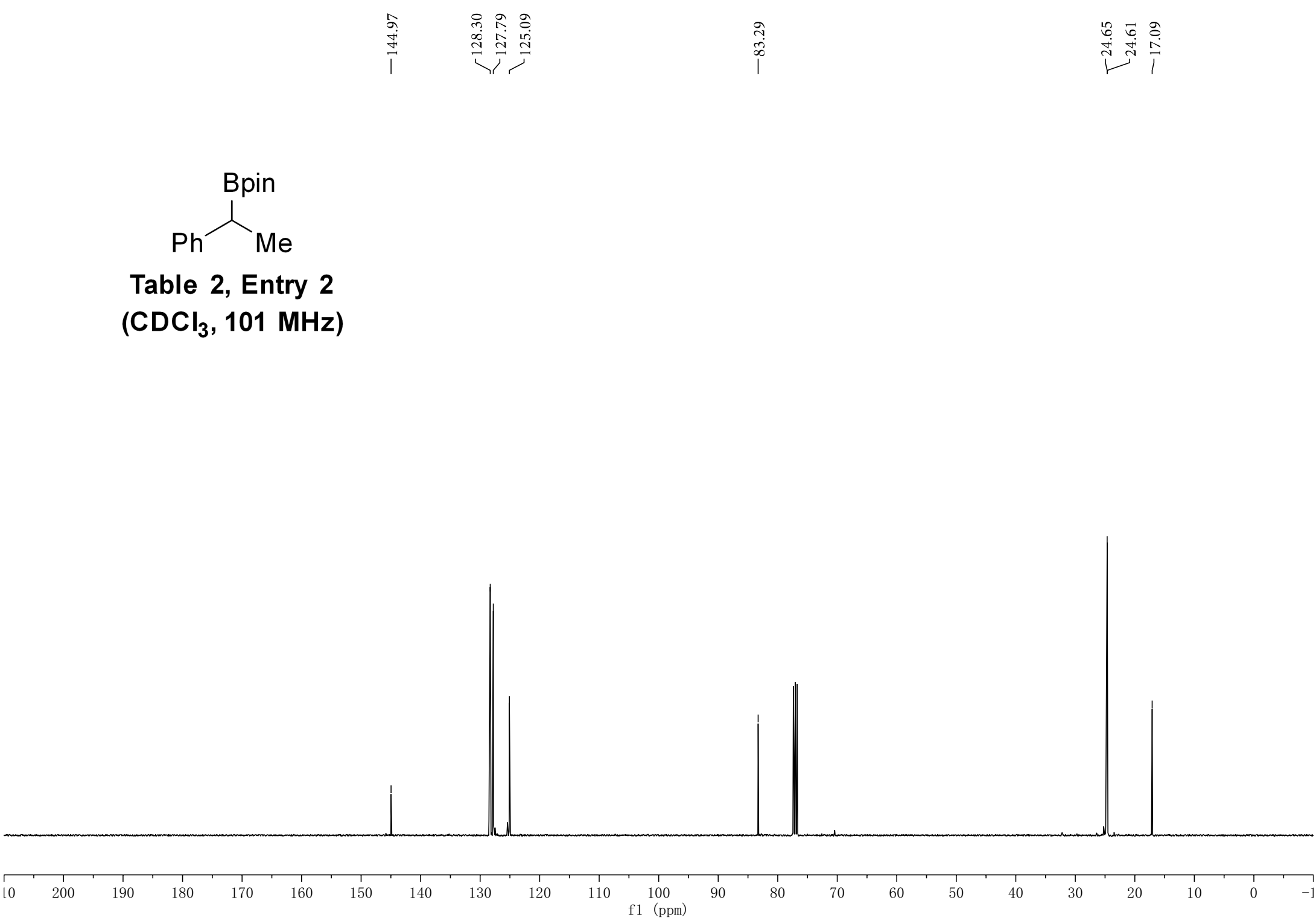
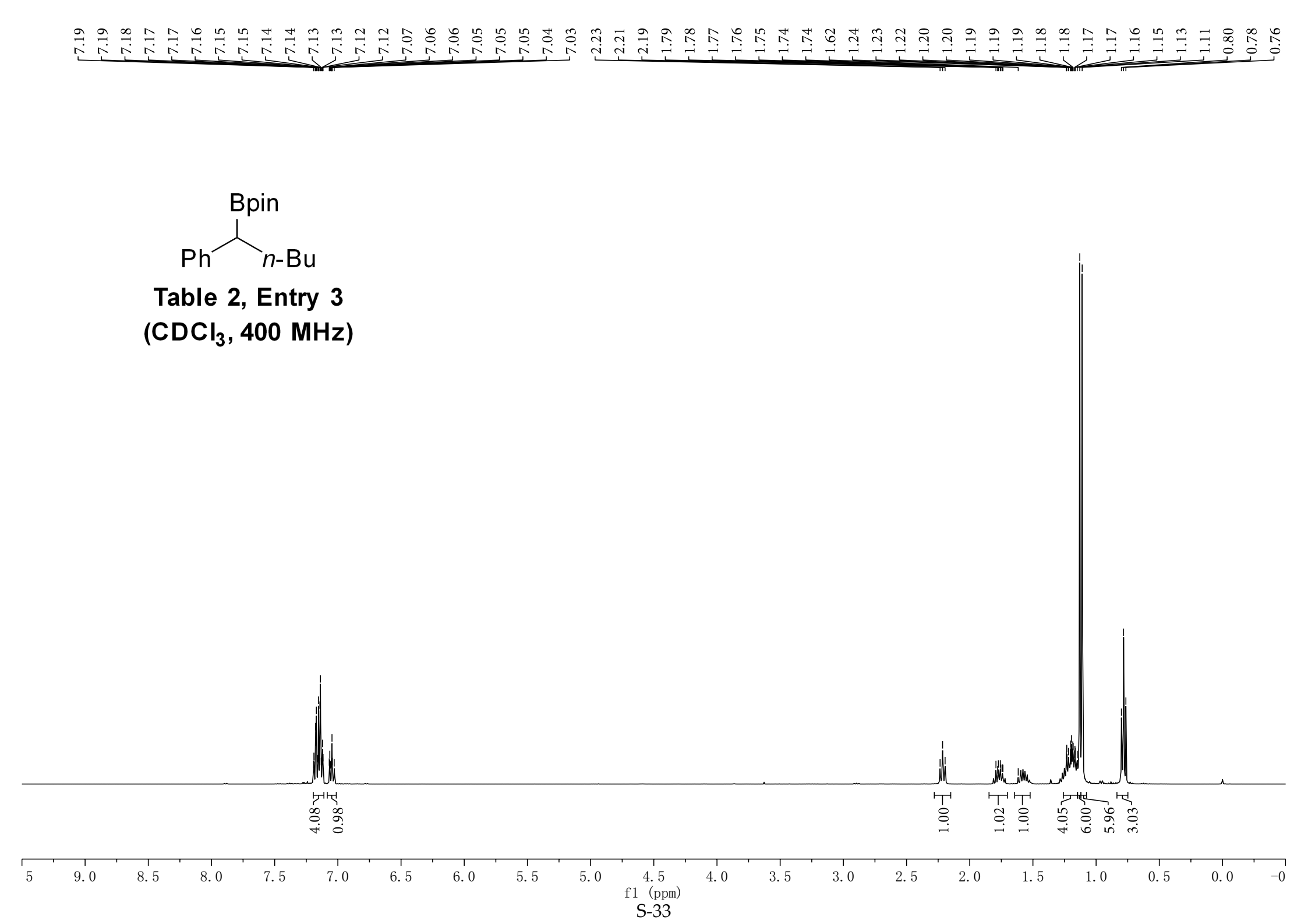
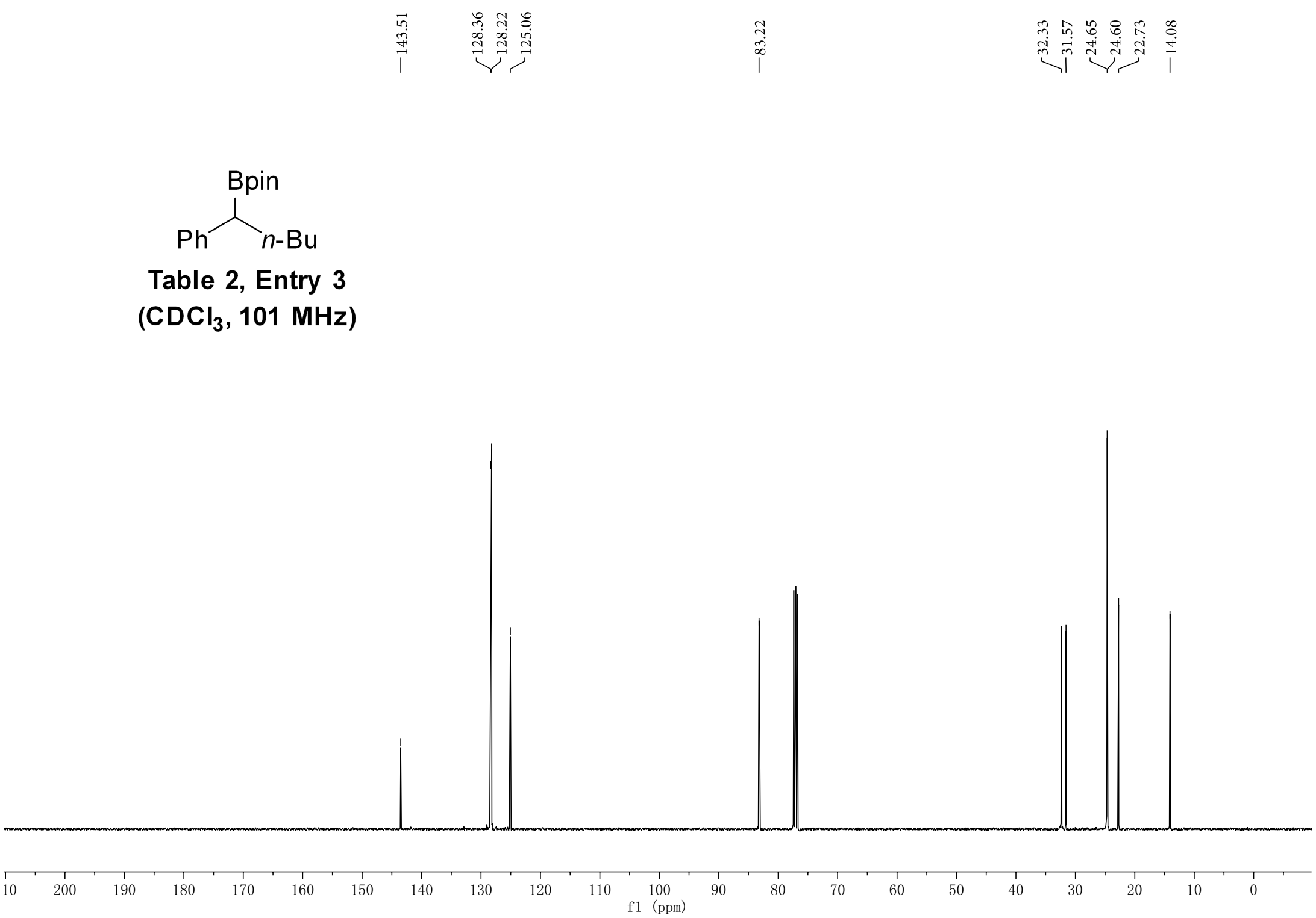


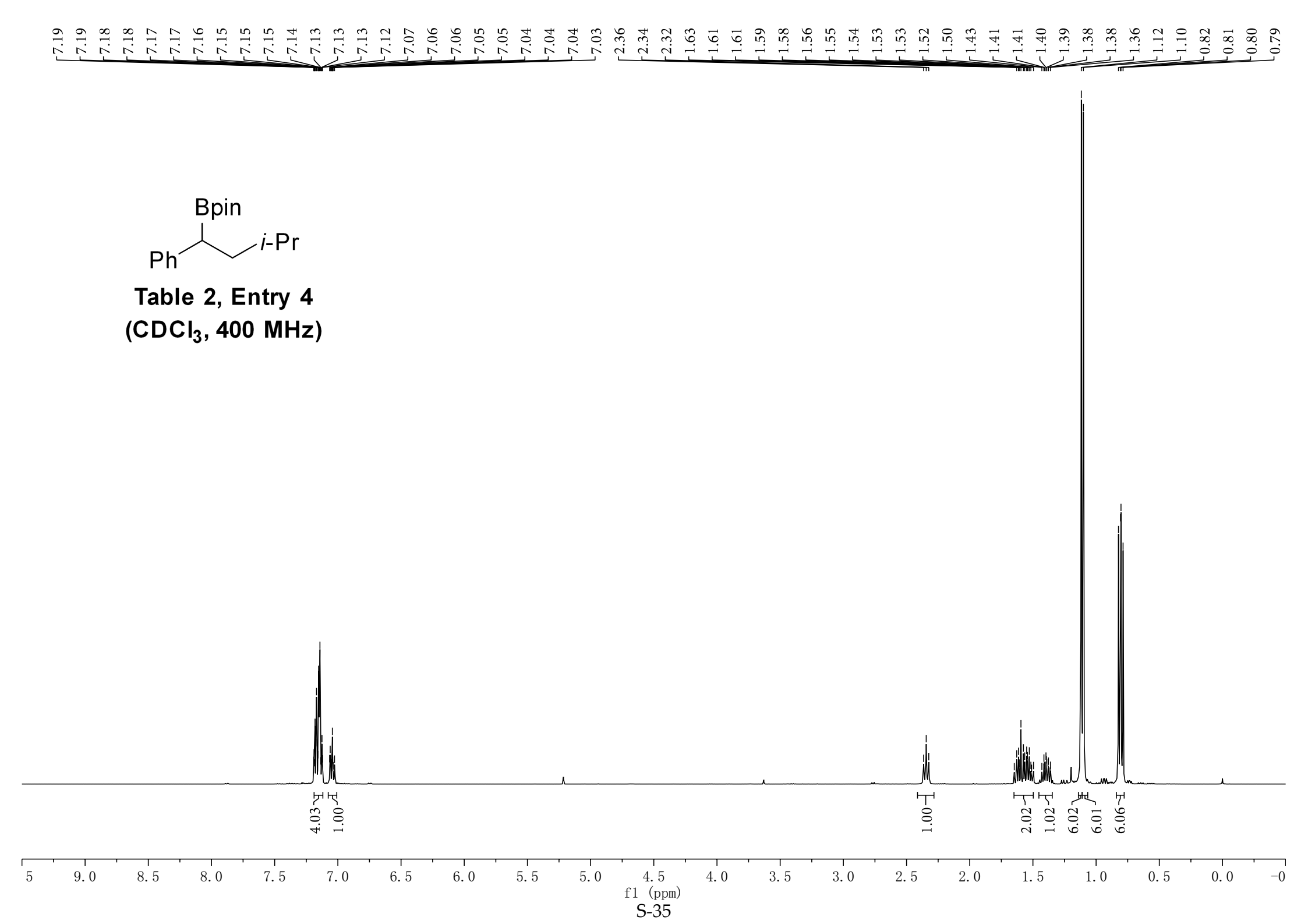

**Table 2, Entry 1**
**($CDCl_3$, 101 MHz)**

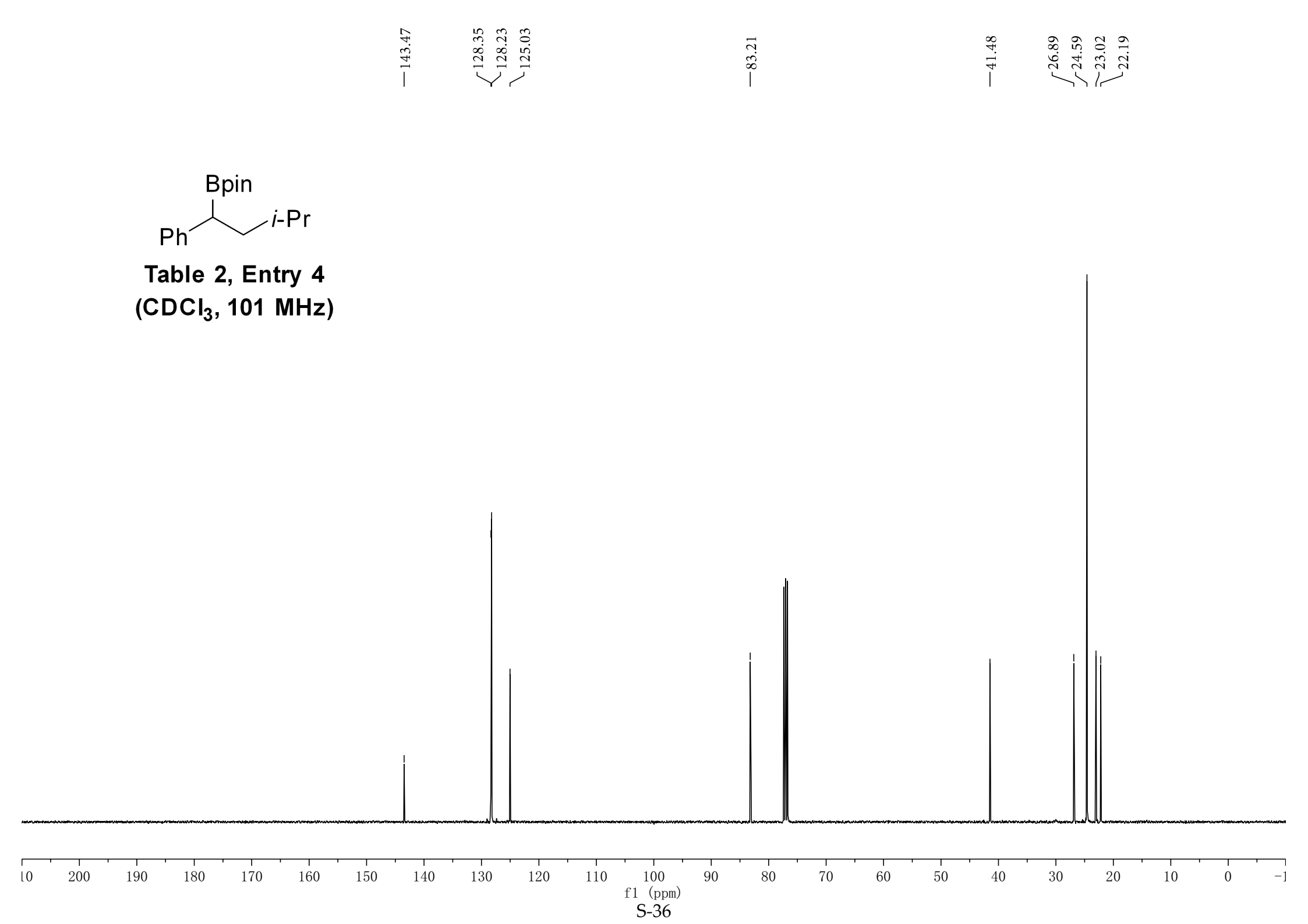

7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.08
7.07
7.06
7.05
7.05
2.39
2.37
2.35
2.33
1.27
1.25
1.14
1.12
Bpin
Ph
Me
Table 2, Entry 2
(CDCl3, 400 MHz)
4.04
0.98
1.00
3.16
6.09
6.02
f1 (ppm)

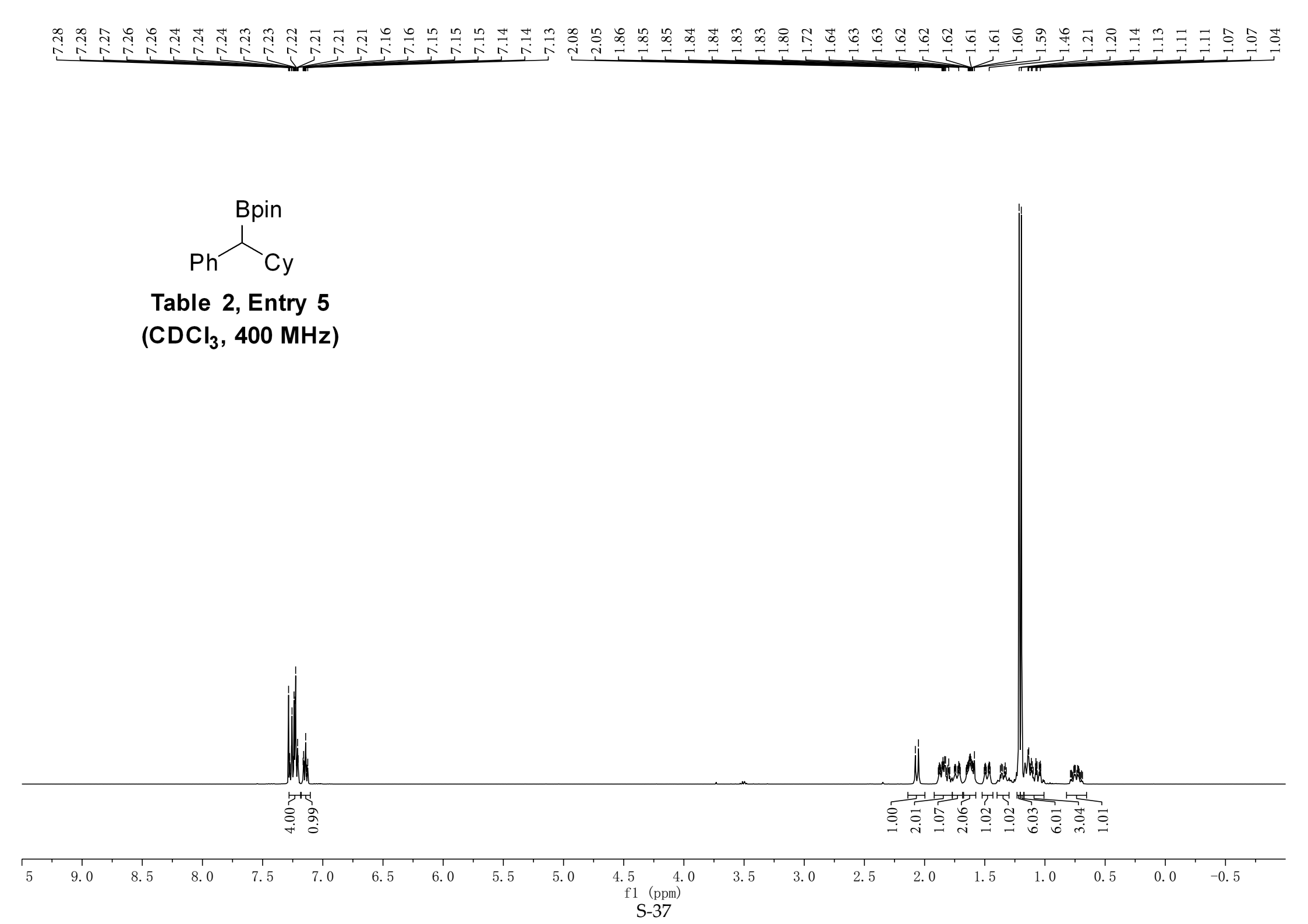

144.97
128.30
127.79
125.09
83.29
24.65
24.61
17.09
Bpin
Ph
Me
Table 2, Entry 2
(CDCl3, 101 MHz)
f1 (ppm)

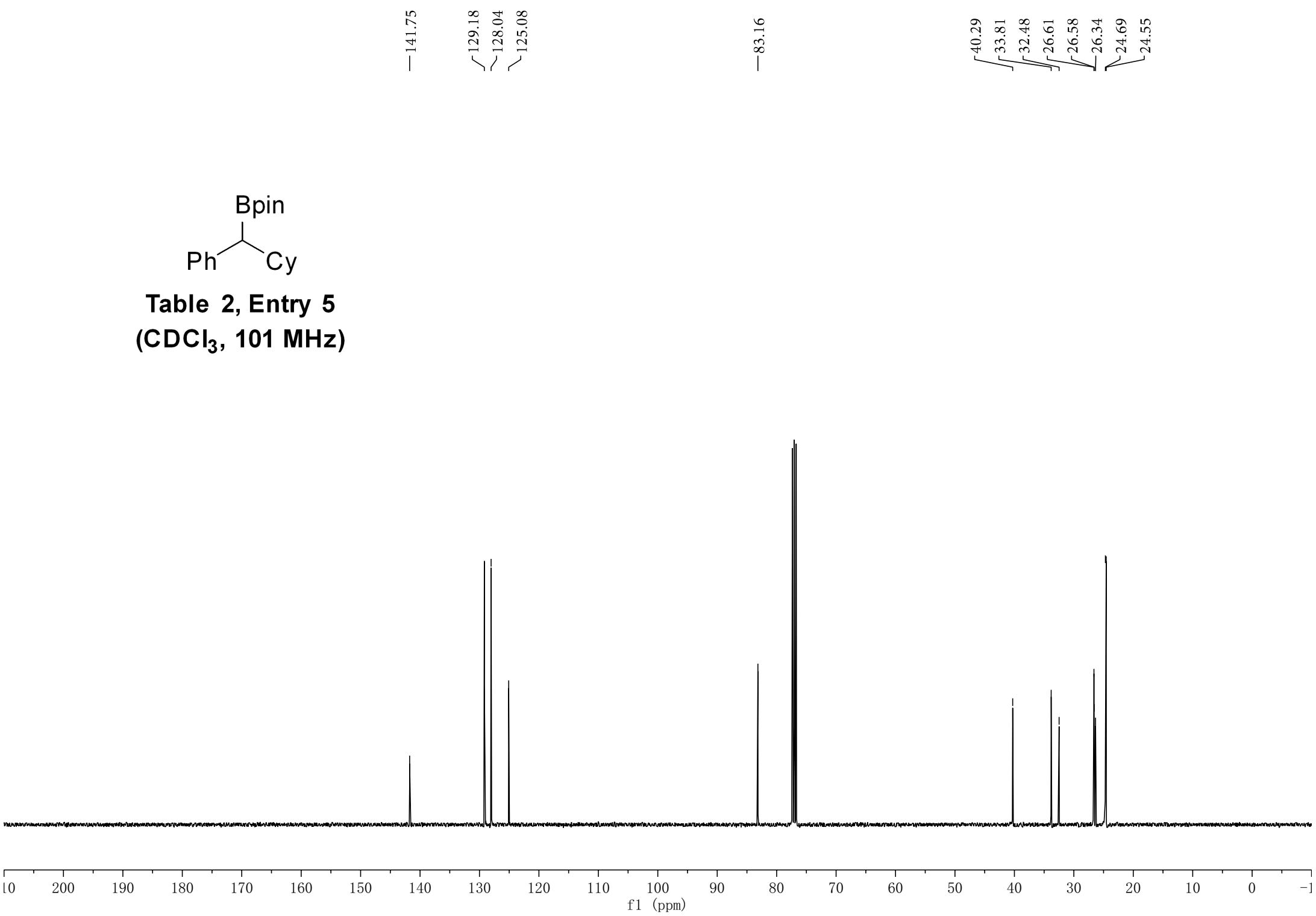

7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.07 7.06 7.06 7.05 7.05 7.05 7.04 7.03
2.23 2.21 2.19 1.79 1.78 1.77 1.76 1.75 1.74 1.74 1.62 1.24 1.23 1.22 1.20 1.20 1.19 1.19 1.19 1.18 1.18 1.17 1.17 1.16 1.15 1.13 1.11 0.80 0.78 0.76
Bpin
Ph
n-Bu
Table 2, Entry 3
(CDCl3, 400 MHz)
4.08 0.98 1.00 1.02 1.00 4.05 6.00 5.96 3.03
f1 (ppm)


143.51
128.36
128.22
125.06
83.22
32.33
31.57
24.65
24.60
22.73
14.08
Bpin
Ph
n-Bu
Table 2, Entry 3
(CDCl3, 101 MHz)
f1 (ppm)


Bpin
Ph
i-Pr
Table 2, Entry 4
(CDCl3, 400 MHz)
f1 (ppm)


143.47
128.35
128.23
125.03
83.21
41.48
26.89
24.59
23.02
22.19
Bpin
Ph
i-Pr
Table 2, Entry 4
(CDCl3, 101 MHz)
f1 (ppm)


7.28 7.28 7.27 7.26 7.26 7.24 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.21 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.13
2.08 2.05 1.86 1.85 1.85 1.84 1.84 1.83 1.83 1.80 1.72 1.64 1.63 1.63 1.62 1.62 1.62 1.61 1.61 1.60 1.59 1.46 1.21 1.20 1.14 1.13 1.11 1.11 1.07 1.07 1.04
Bpin
Ph
Cy
Table 2, Entry 5
(CDCl3, 400 MHz)
4.00 0.99
1.00 2.01 1.07 2.06 1.02 1.02 6.03 6.01 3.04 1.01
f1 (ppm)


141.75
129.18
128.04
125.08
83.16
40.29
33.81
32.48
26.61
26.58
26.34
24.69
24.55
Bpin
Ph
Cy
Table 2, Entry 5
(CDCl3, 101 MHz)
f1 (ppm)

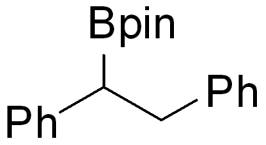
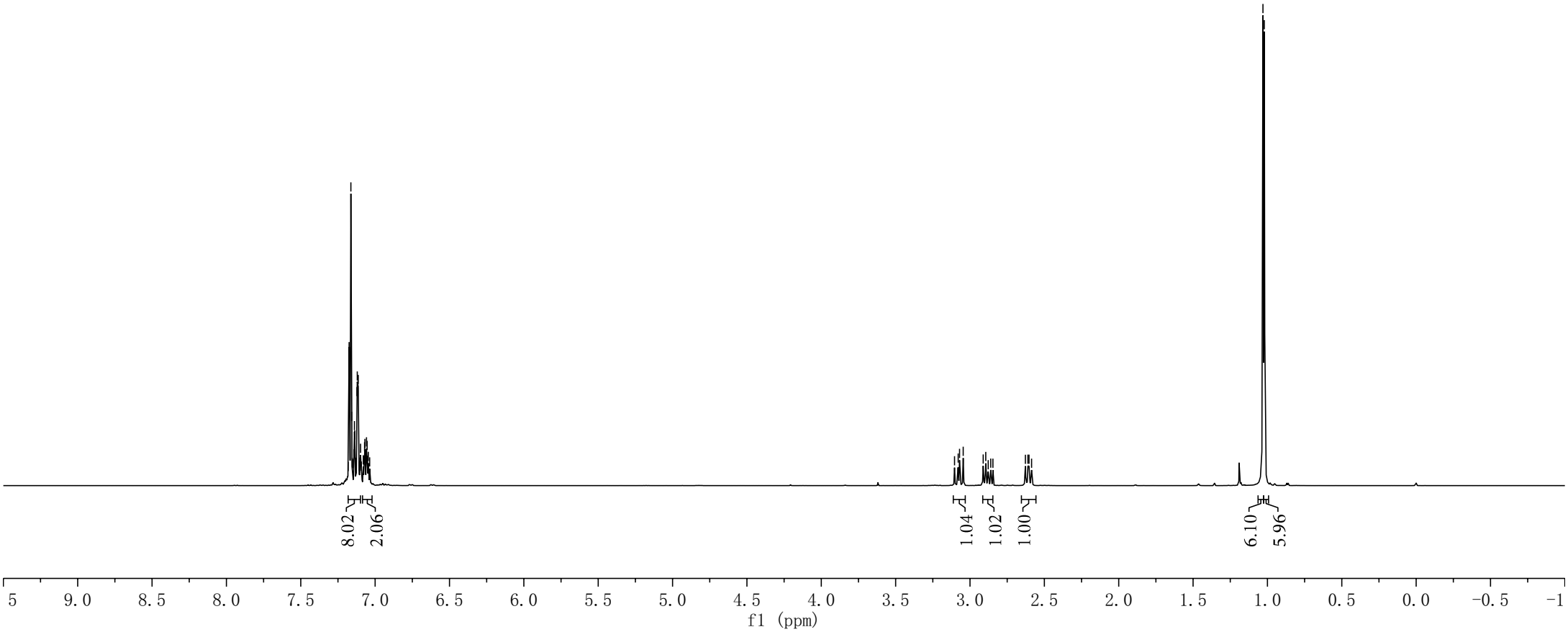




**Table 2, Entry 6**
**($CDCl_3$, 400 MHz)**



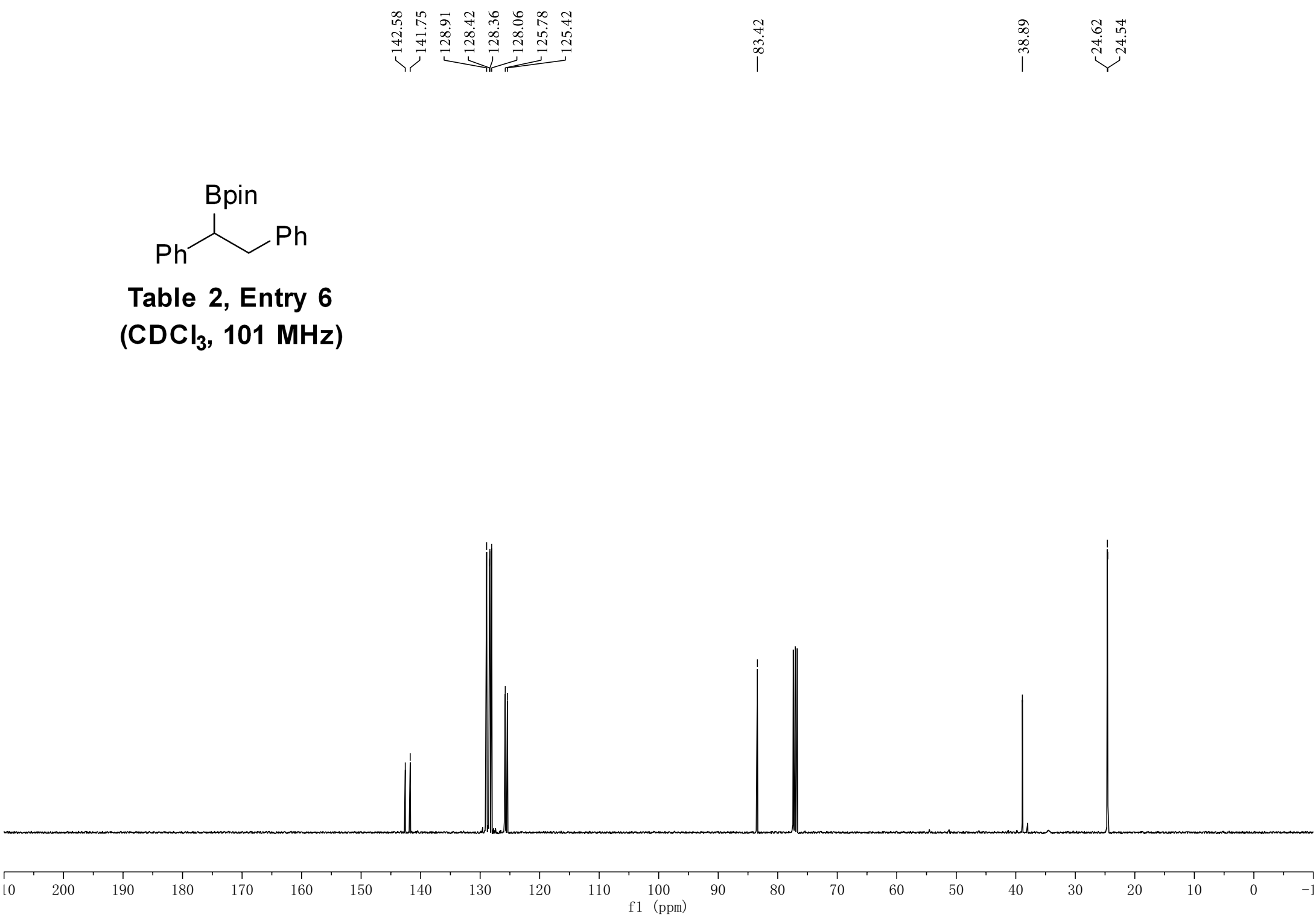
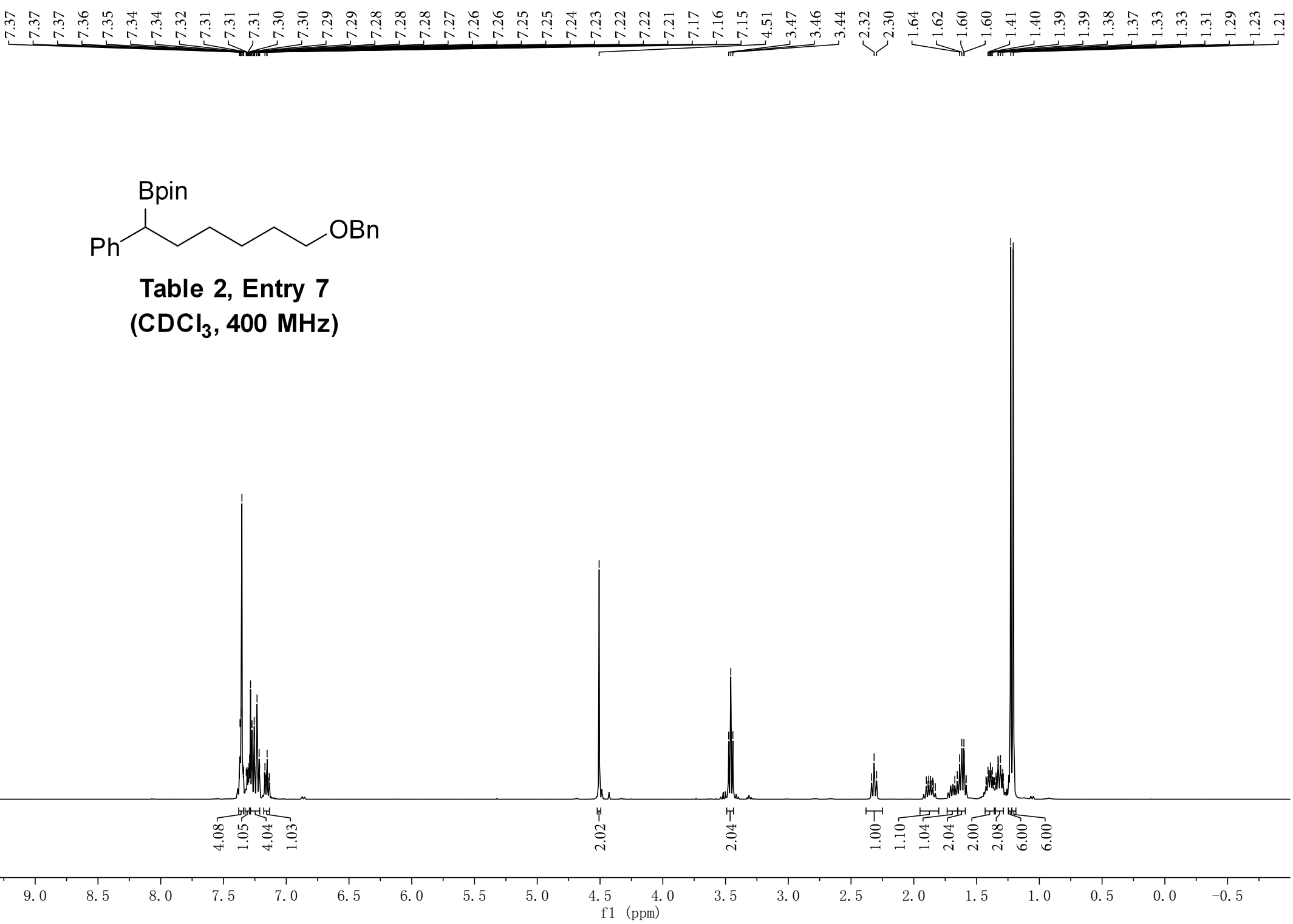
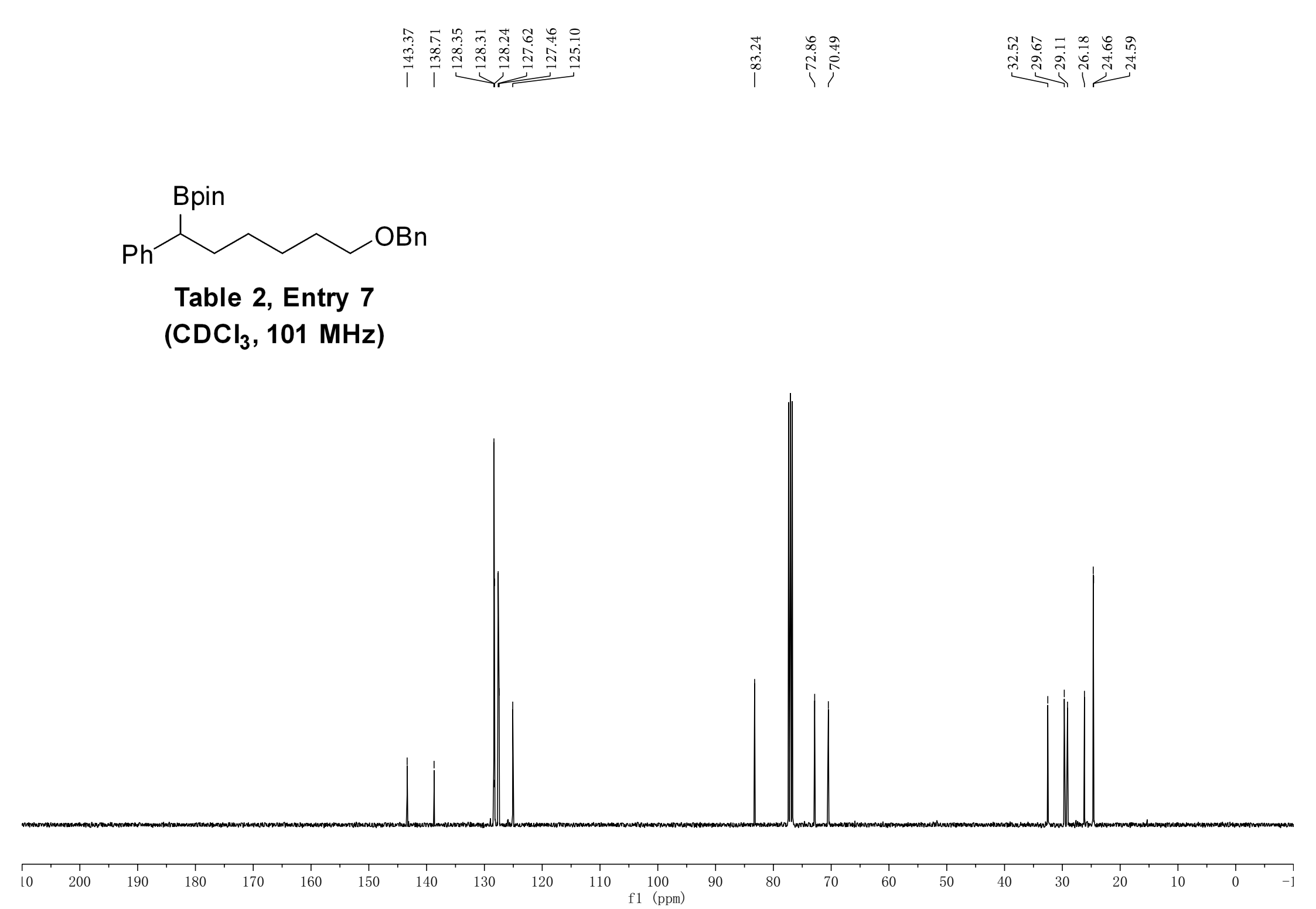
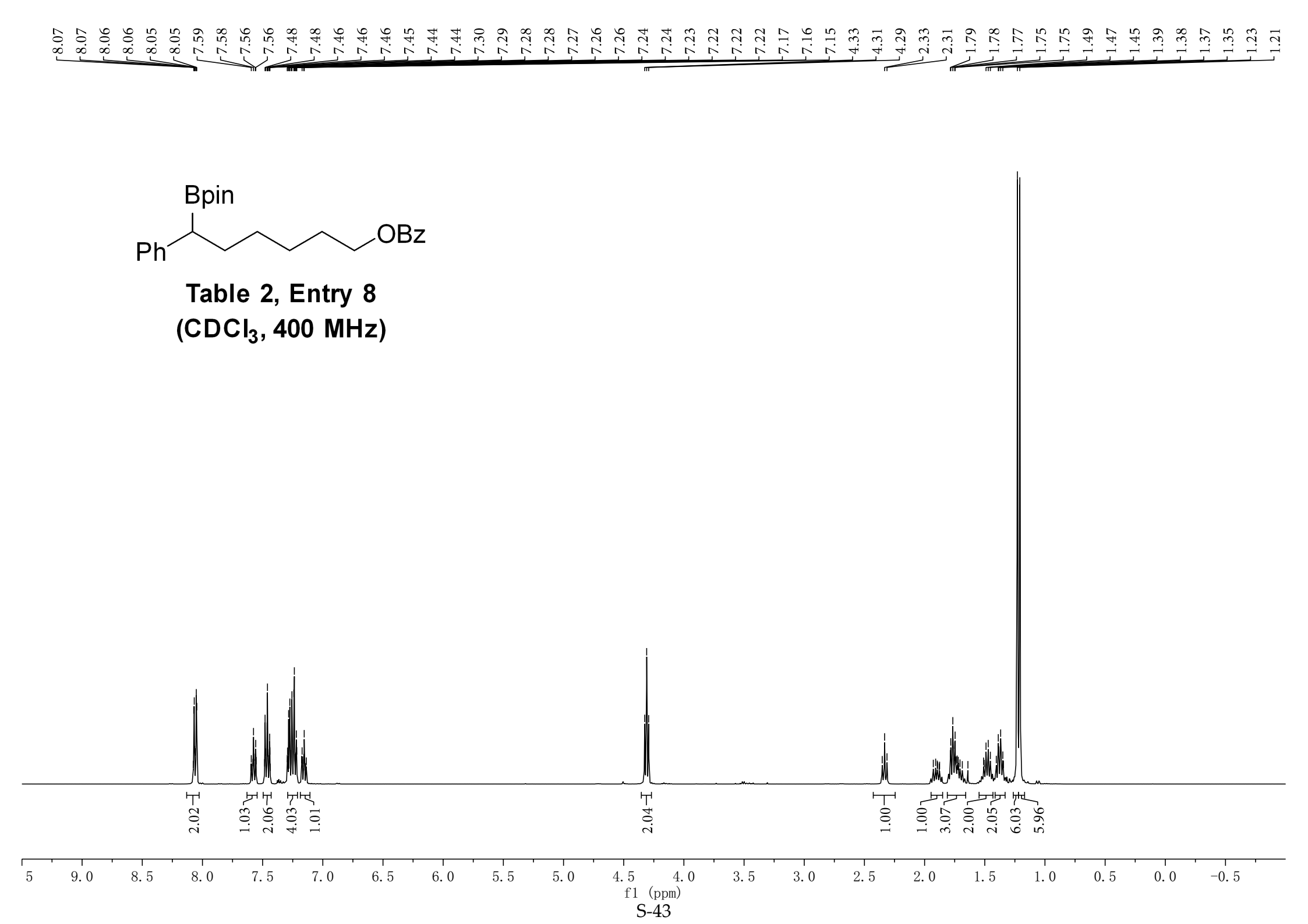



**Table 2, Entry 6**
**($CDCl_3$, 101 MHz)**


7.37 7.37 7.37 7.36 7.35 7.34 7.34 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.17 7.16 7.15 4.51 3.47 3.46 3.44 2.32 2.30 1.64 1.62 1.60 1.60 1.41 1.40 1.39 1.39 1.38 1.37 1.33 1.33 1.31 1.29 1.23 1.21
Bpin
Ph
OBn
Table 2, Entry 7
(CDCl3, 400 MHz)
4.08 1.05 4.04 1.03 2.02 2.04 1.00 1.10 1.04 2.04 2.00 2.08 6.00 6.00
f1 (ppm)


143.37
138.71
128.35
128.31
128.24
127.62
127.46
125.10
83.24
72.86
70.49
32.52
29.67
29.11
26.18
24.66
24.59
Bpin
Ph
OBn
Table 2, Entry 7
(CDCl3, 101 MHz)
f1 (ppm)


Bpin
Ph
OBz
Table 2, Entry 8
(CDCl3, 400 MHz)
8.07 8.07 8.06 8.06 8.05 8.05 7.59 7.58 7.56 7.56 7.48 7.48 7.46 7.46 7.46 7.45 7.44 7.44 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.24 7.24 7.23 7.22 7.22 7.22 7.17 7.16 7.15 4.33 4.31 4.29 2.33 2.31 1.79 1.78 1.77 1.75 1.75 1.49 1.47 1.45 1.39 1.38 1.37 1.35 1.23 1.21
2.02 1.03 2.06 4.03 1.01 2.04 1.00 1.00 3.07 2.00 2.05 6.03 5.96
f1 (ppm)

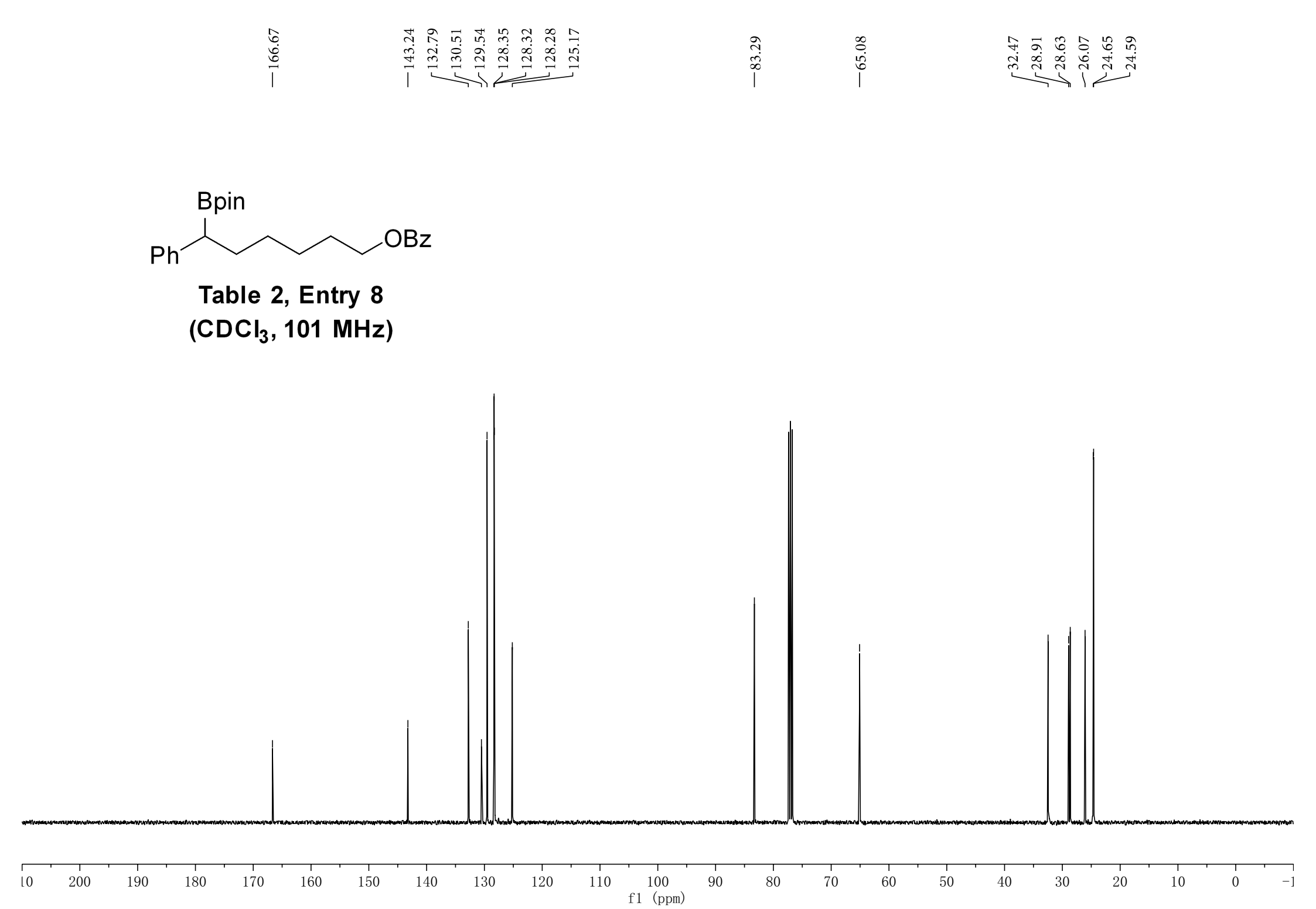
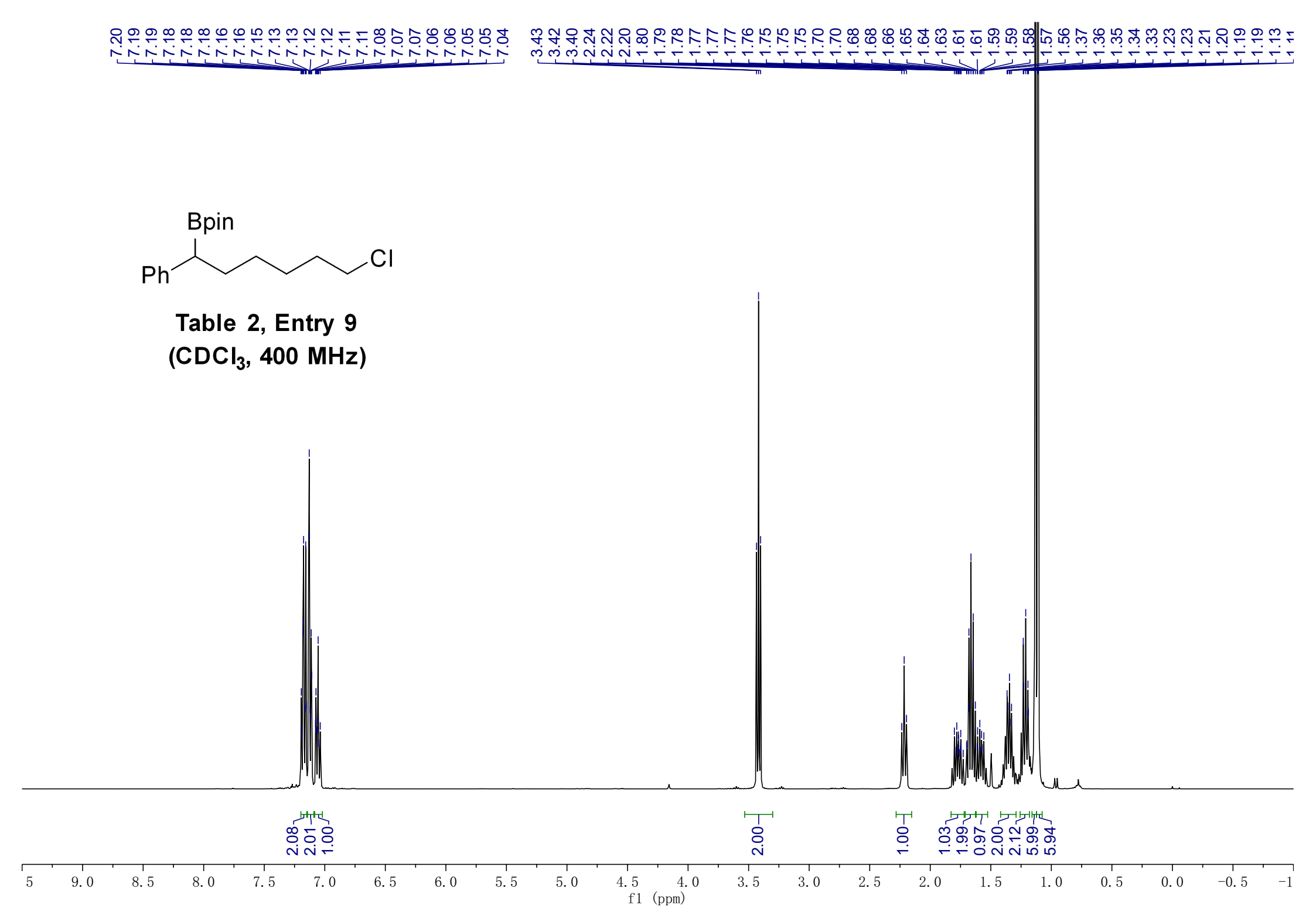
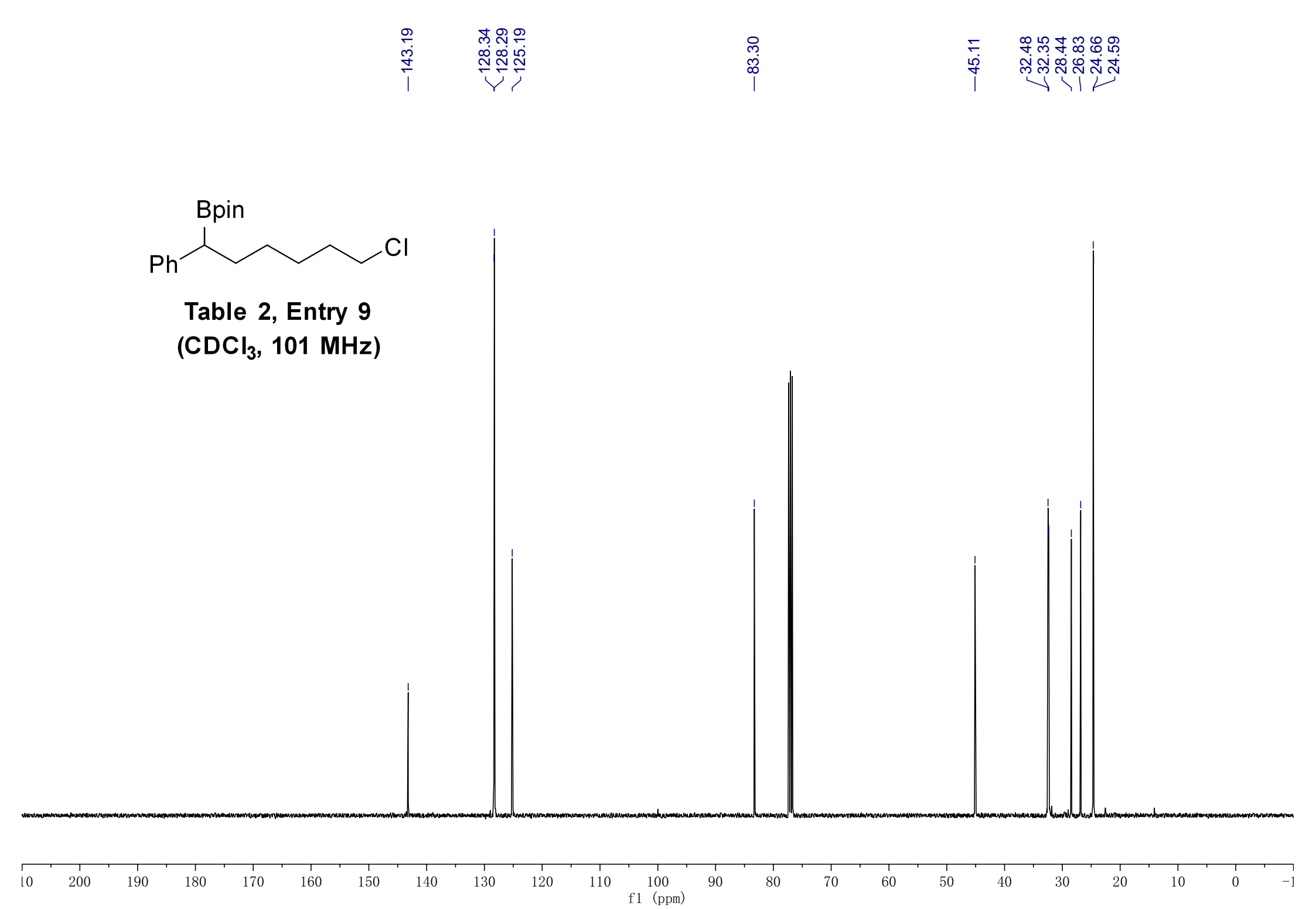



**Table 2, Entry 8**
**($CDCl_3$, 101 MHz)**


Bpin
Ph
Cl
Table 2, Entry 9
(CDCl3, 400 MHz)
f1 (ppm)


143.19
128.34
128.29
125.19
83.30
45.11
32.48
32.35
28.44
26.83
24.66
24.59
Bpin
Ph
Cl
Table 2, Entry 9
(CDCl3, 101 MHz)
f1 (ppm)

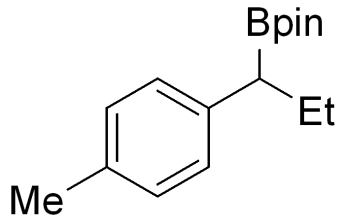
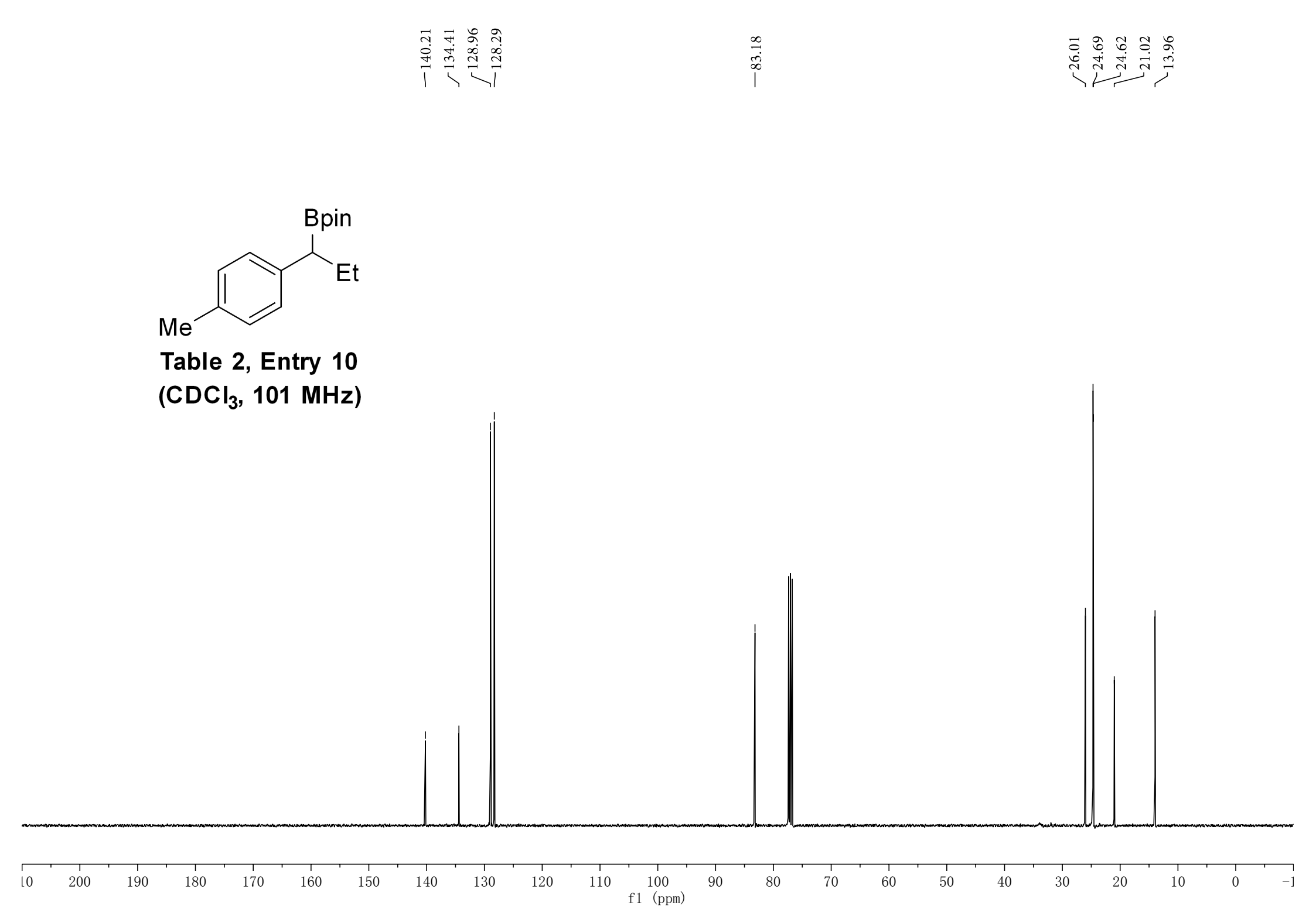
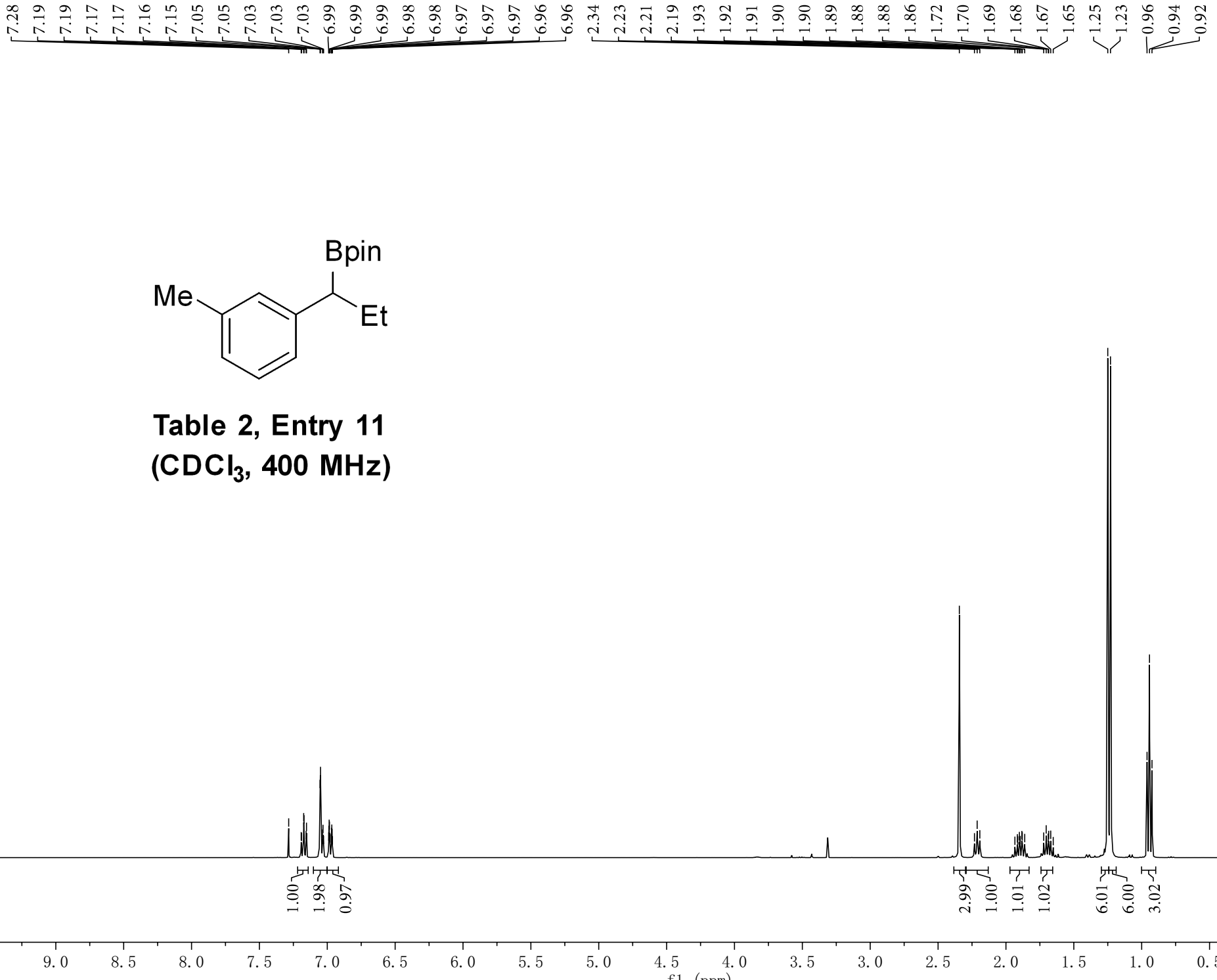



**Table 2, Entry 10**
**($CDCl_3$, 400 MHz)**


140.21
134.41
128.96
128.29
83.18
26.01
24.69
24.62
21.02
13.96
Bpin
Et
Me
Table 2, Entry 10
(CDCl3, 101 MHz)
f1 (ppm)


7.28
7.19
7.19
7.17
7.17
7.16
7.15
7.05
7.05
7.03
7.03
7.03
6.99
6.99
6.99
6.98
6.98
6.97
6.97
6.97
6.96
6.96
2.34
2.23
2.21
2.19
1.93
1.92
1.91
1.90
1.90
1.89
1.88
1.88
1.86
1.72
1.70
1.69
1.68
1.67
1.65
1.25
1.23
0.96
0.94
0.92
Bpin
Me
Et
Table 2, Entry 11
(CDCl3, 400 MHz)
1.00
1.98
0.97
2.99
1.00
1.01
1.02
6.01
6.00
3.02
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

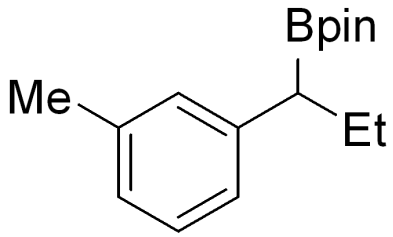
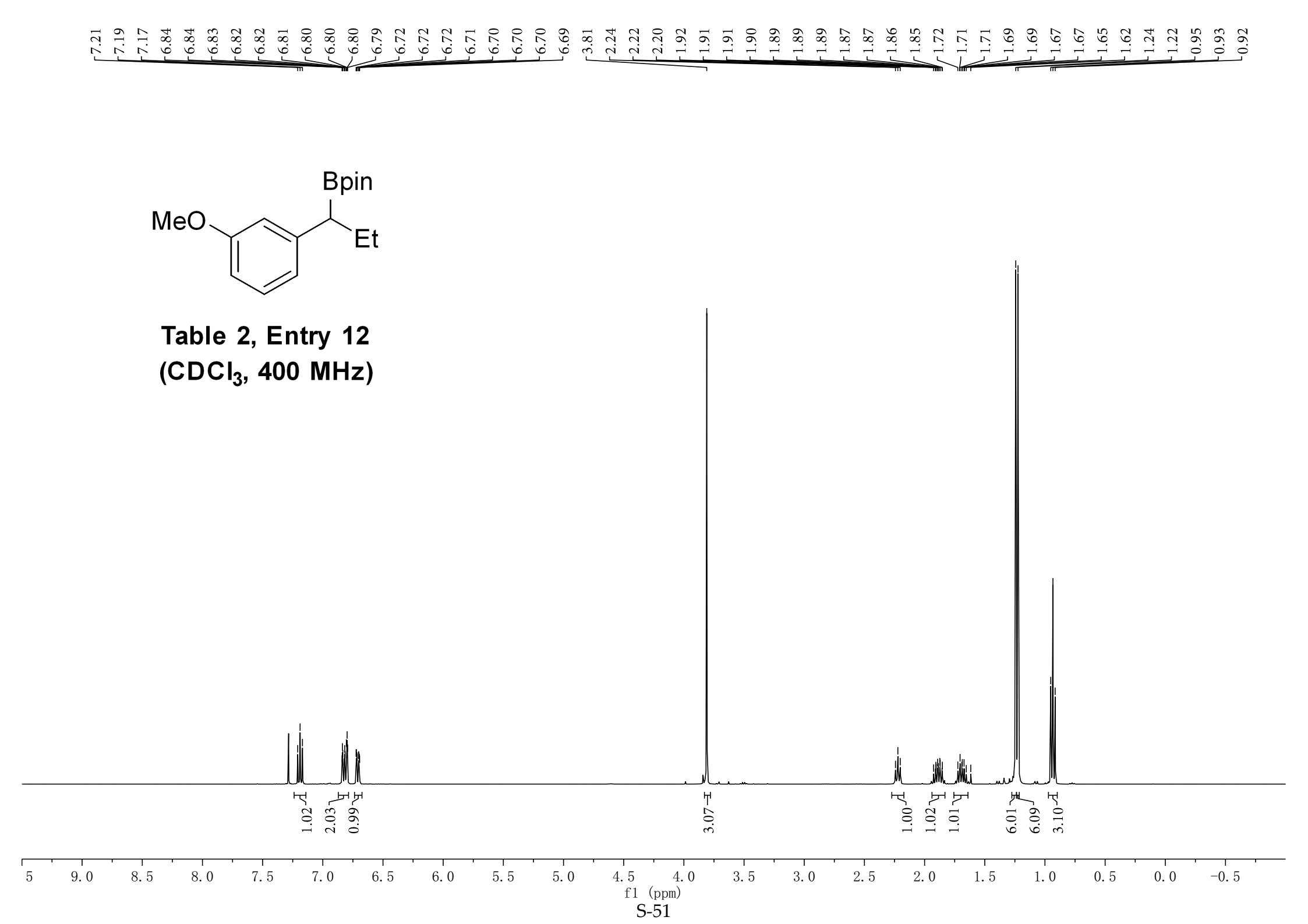



**Table 2, Entry 11**
**($CDCl_3$, 101 MHz)**


7.21
7.19
7.17
6.84
6.84
6.83
6.82
6.82
6.81
6.80
6.80
6.80
6.79
6.72
6.72
6.72
6.71
6.70
6.70
6.70
6.69
3.81
2.24
2.22
2.20
1.92
1.91
1.91
1.90
1.89
1.89
1.89
1.87
1.87
1.86
1.85
1.72
1.71
1.71
1.69
1.69
1.67
1.67
1.65
1.62
1.24
1.22
0.95
0.93
0.92
Bpin
MeO
Et
Table 2, Entry 12
(CDCl3, 400 MHz)
1.02
2.03
0.99
3.07
1.00
1.02
1.01
6.01
6.09
3.10
f1 (ppm)

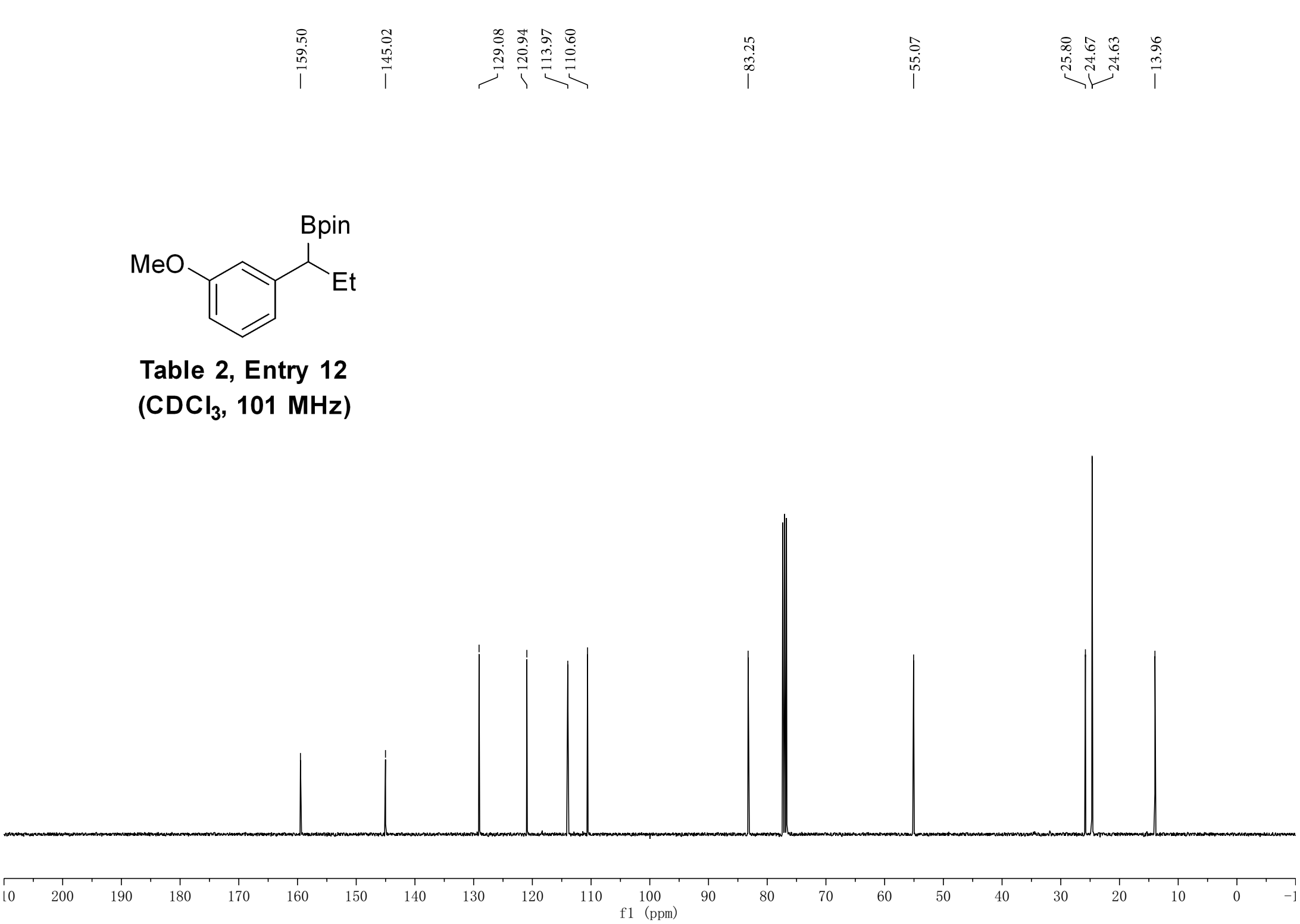



**Table 2, Entry 12**
**($CDCl_3$, 101 MHz)**

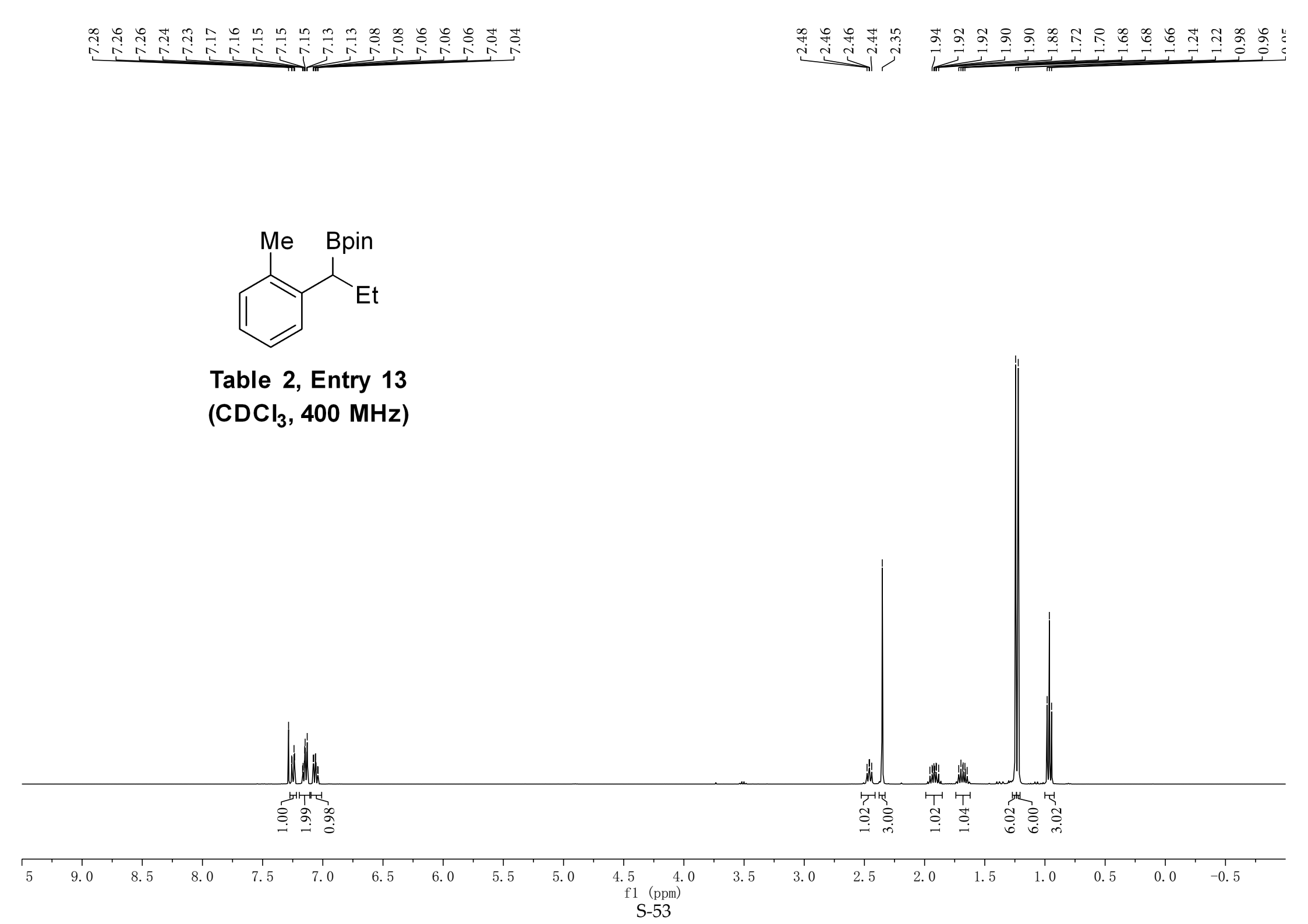



**Table 2, Entry 13**
**($CDCl_3$, 400 MHz)**

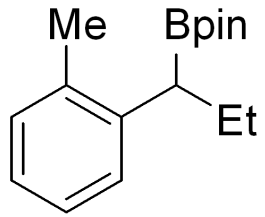



**Table 2, Entry 13**
**($CDCl_3$, 101 MHz)**

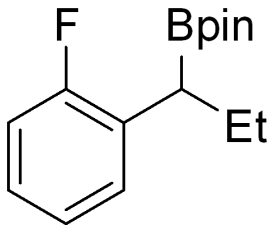



**Table 2, Entry 14**
**($CDCl_3$, 400 MHz)**

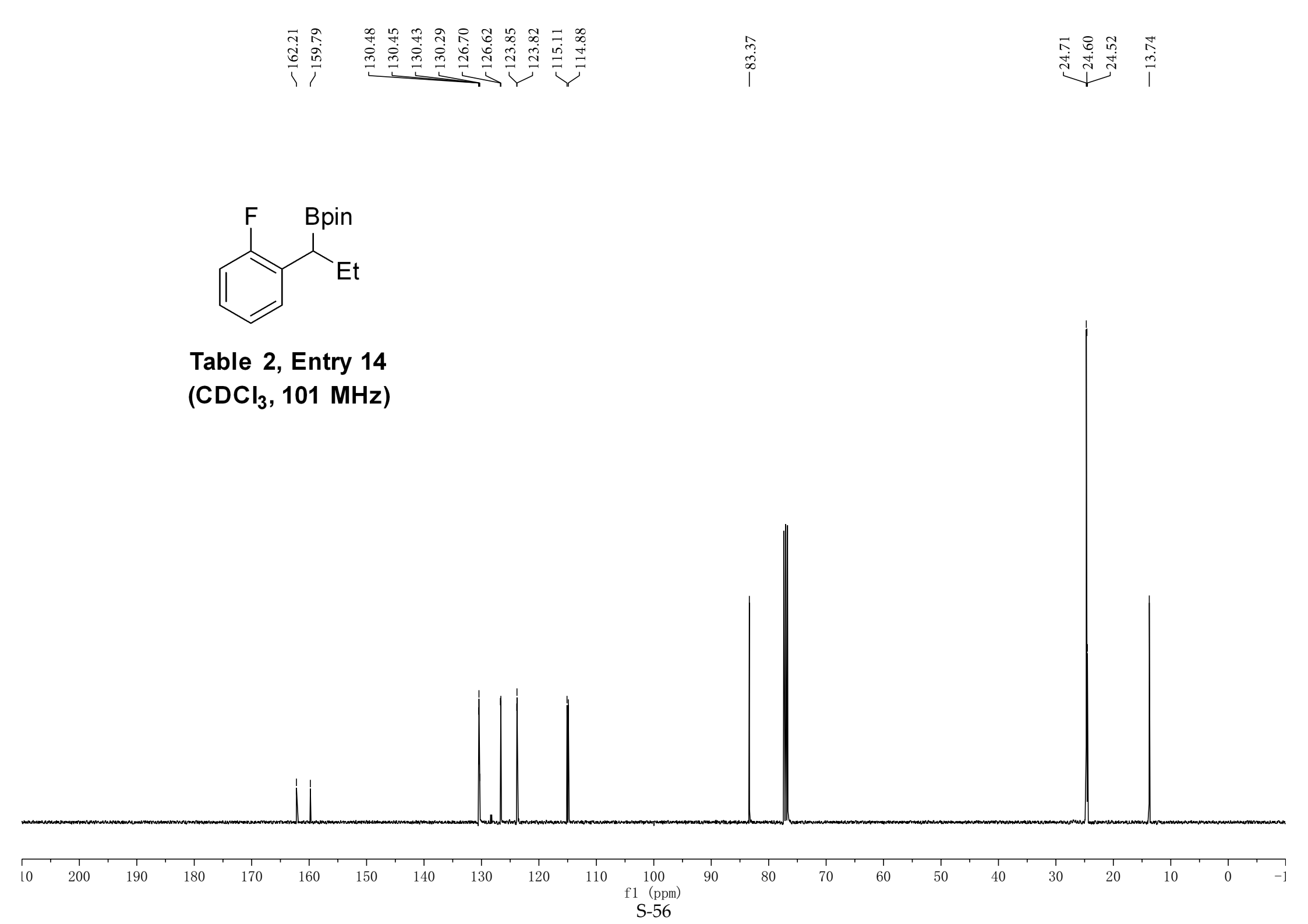
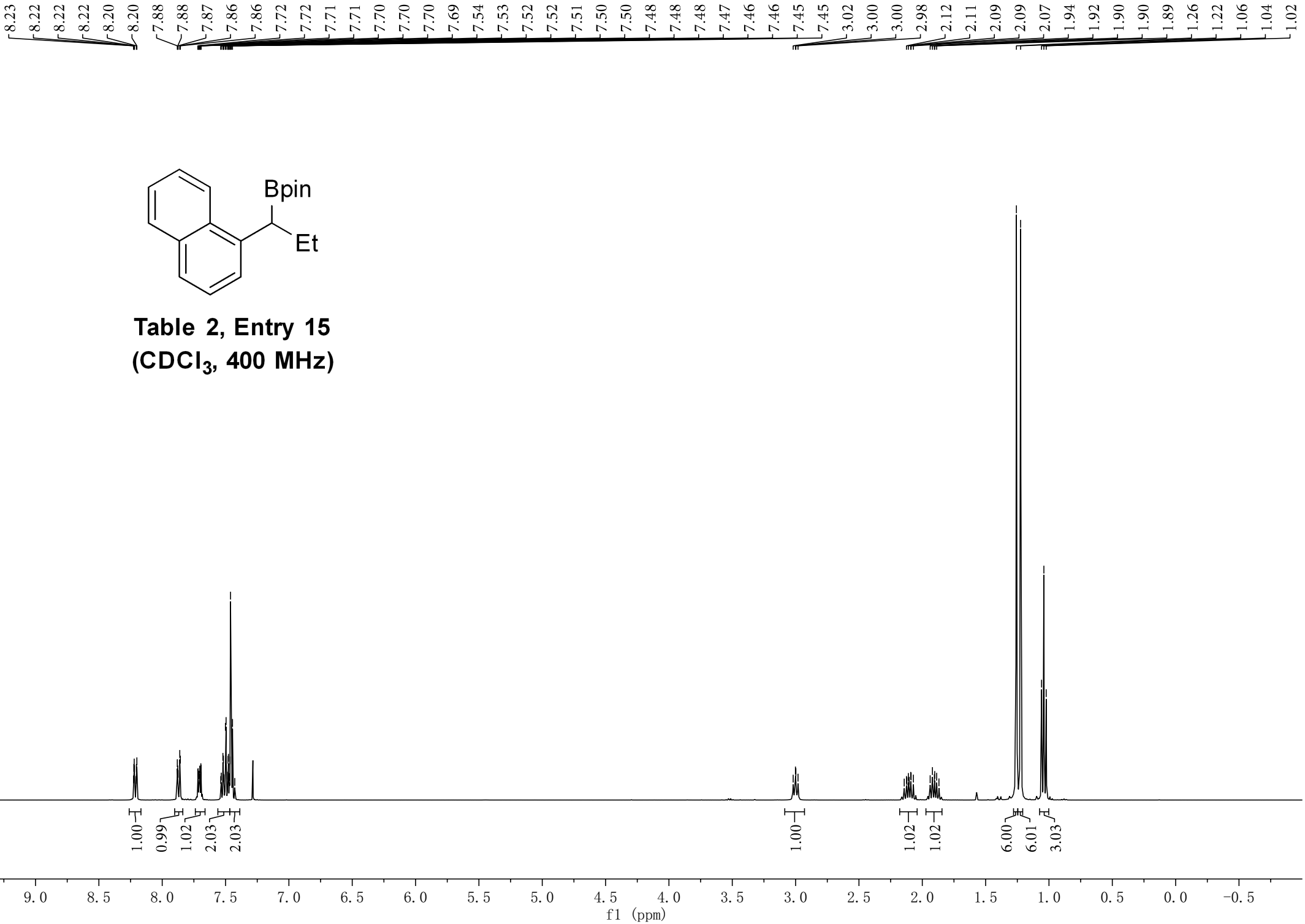



**Table 2, Entry 14**
**($CDCl_3$, 101 MHz)**


8.23 8.22 8.22 8.22 8.20 8.20 7.88 7.88 7.87 7.86 7.86 7.72 7.72 7.71 7.71 7.70 7.70 7.70 7.69 7.54 7.53 7.52 7.52 7.51 7.50 7.50 7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.45 3.02 3.00 3.00 2.98 2.12 2.11 2.09 2.09 2.07 1.94 1.92 1.90 1.90 1.89 1.26 1.22 1.06 1.04 1.02
Bpin
Et
Table 2, Entry 15
(CDCl3, 400 MHz)
1.00 0.99 1.02 2.03 2.03 1.00 1.02 1.02 6.00 6.01 3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

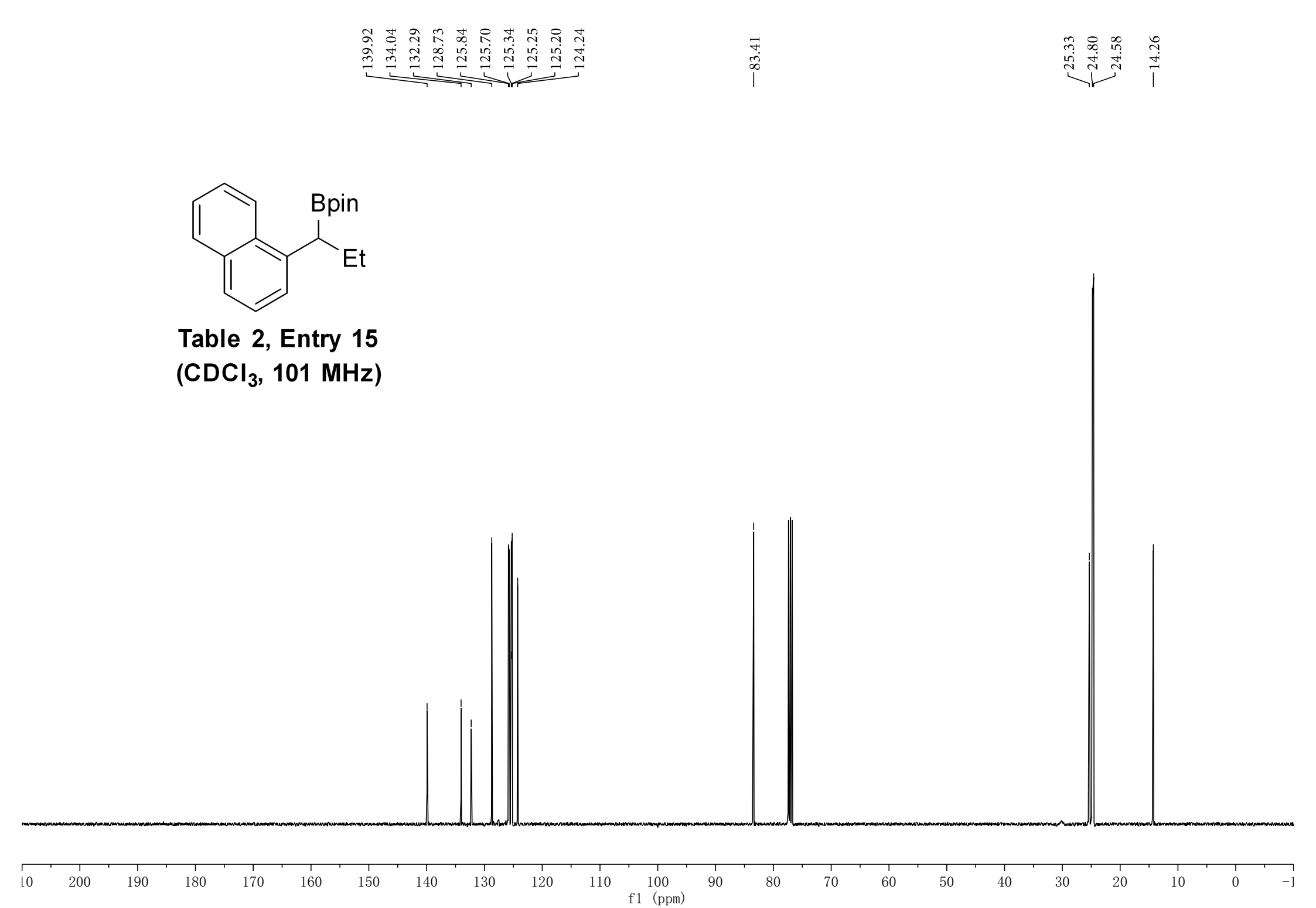



**Table 2, Entry 15**
**($CDCl_3$, 101 MHz)**

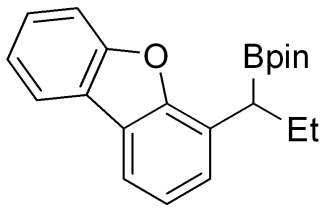



**Table 2, Entry 16**
**($CDCl_3$, 400 MHz)**

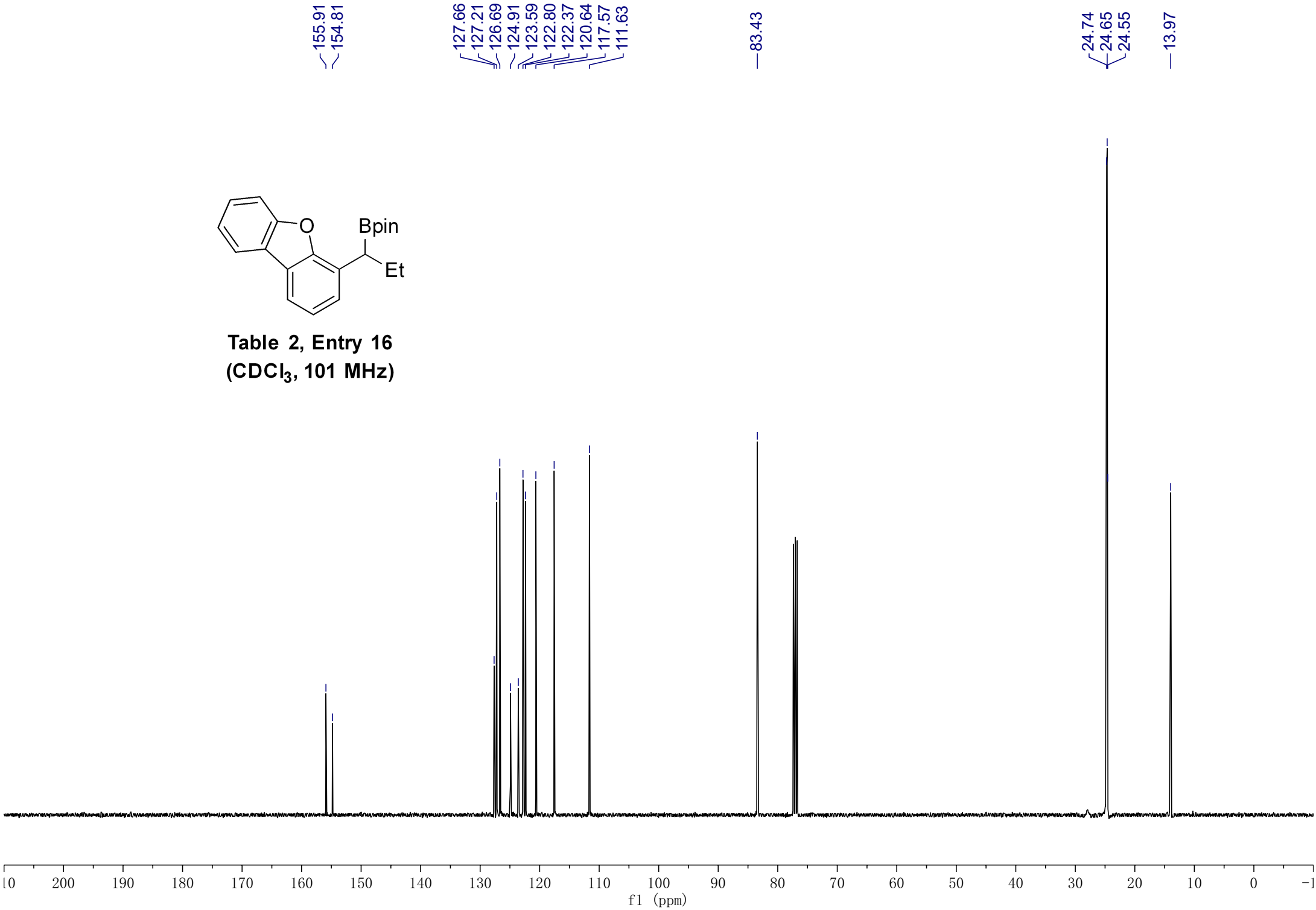
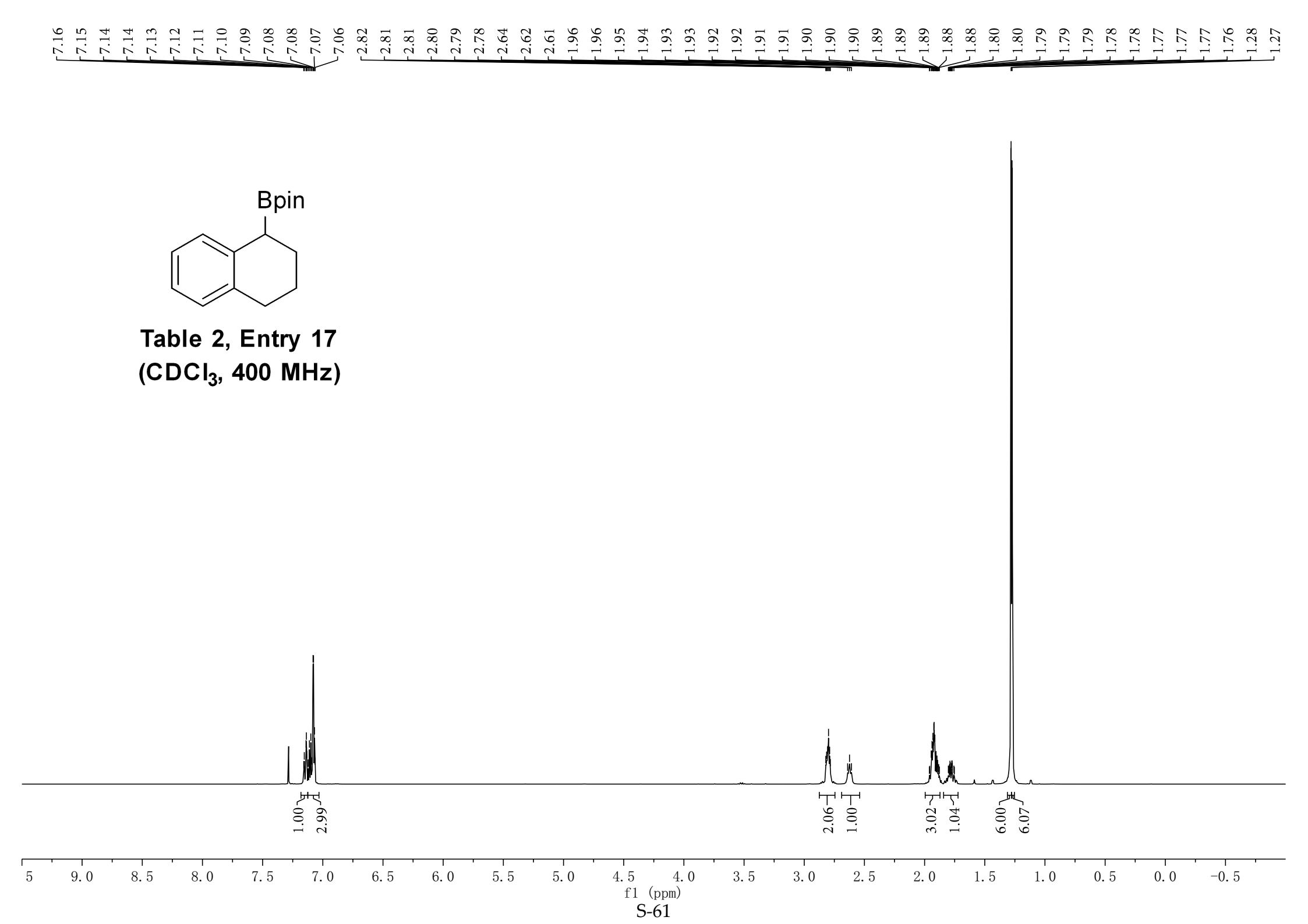
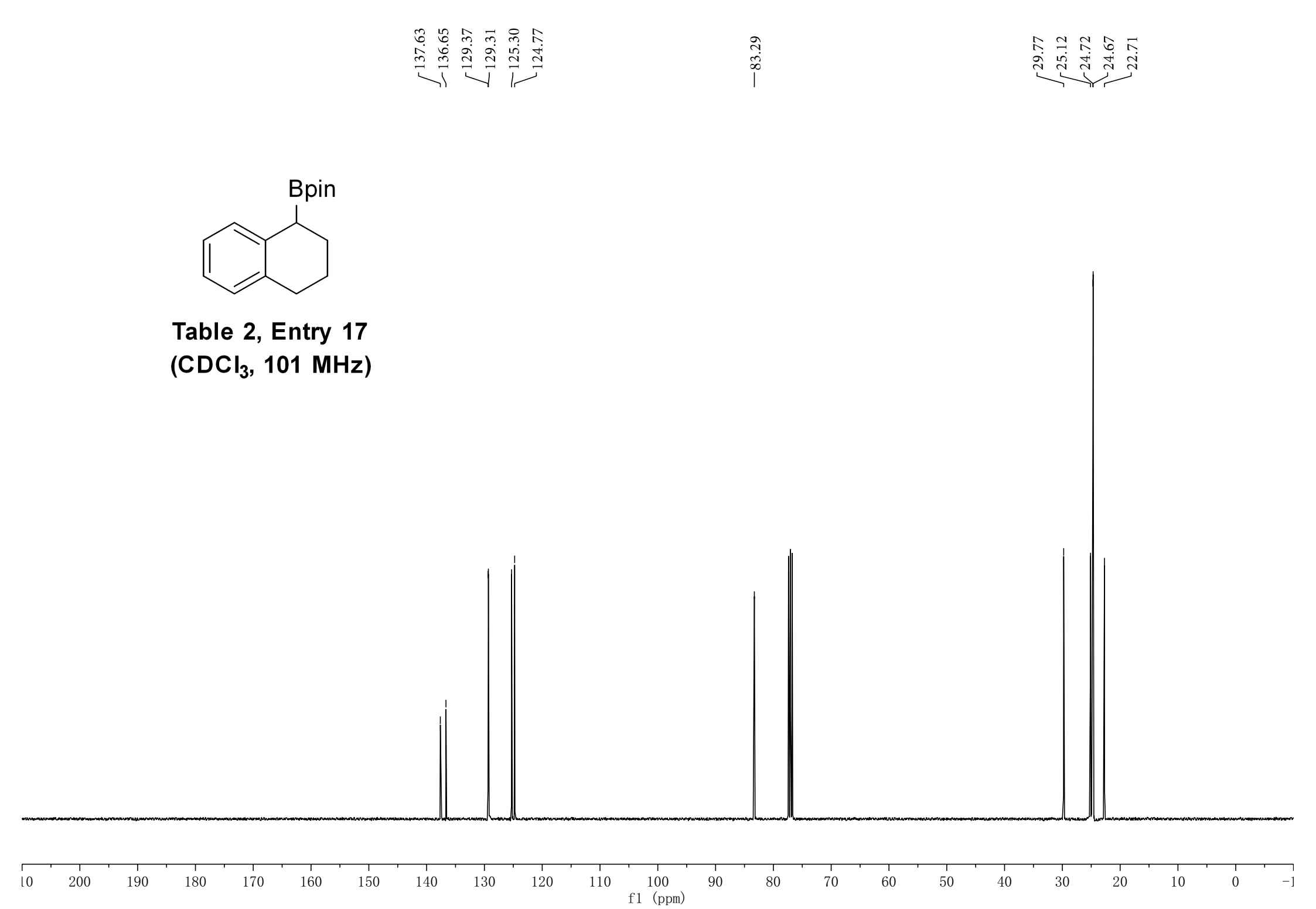



**Table 2, Entry 16**
**($CDCl_3$, 101 MHz)**


7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.08
7.07
7.06
2.82
2.81
2.81
2.80
2.79
2.78
2.64
2.62
2.61
1.96
1.96
1.95
1.94
1.93
1.93
1.92
1.92
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.89
1.88
1.88
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.77
1.77
1.77
1.76
1.28
1.27
Bpin
Table 2, Entry 17
(CDCl3, 400 MHz)
1.00
2.99
2.06
1.00
3.02
1.04
6.00
6.07
5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.63
136.65
129.37
129.31
125.30
124.77
83.29
29.77
25.12
24.72
24.67
22.71
Bpin
Table 2, Entry 17
(CDCl3, 101 MHz)
f1 (ppm)

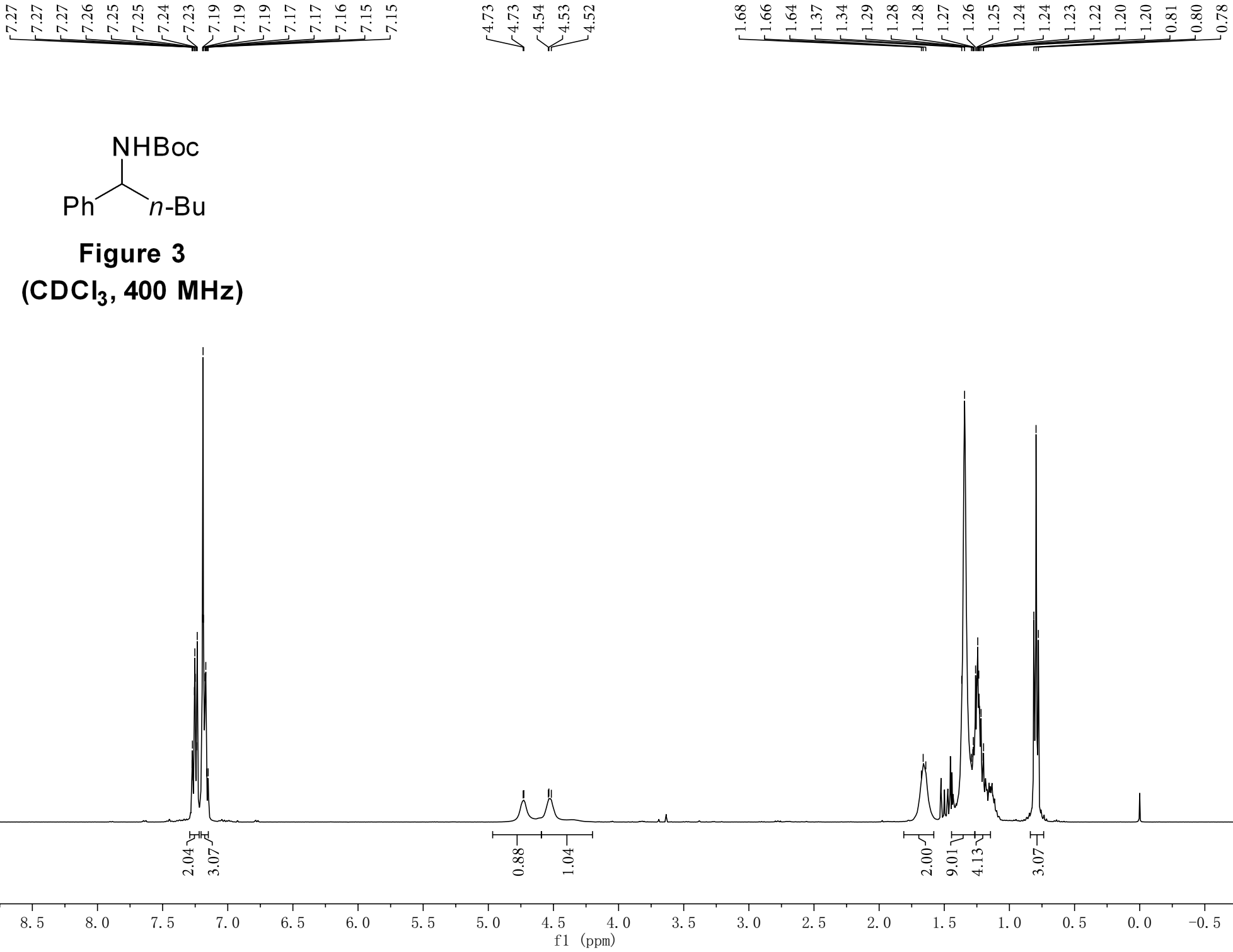



**Figure 3**
**($CDCl_3$, 400 MHz)**

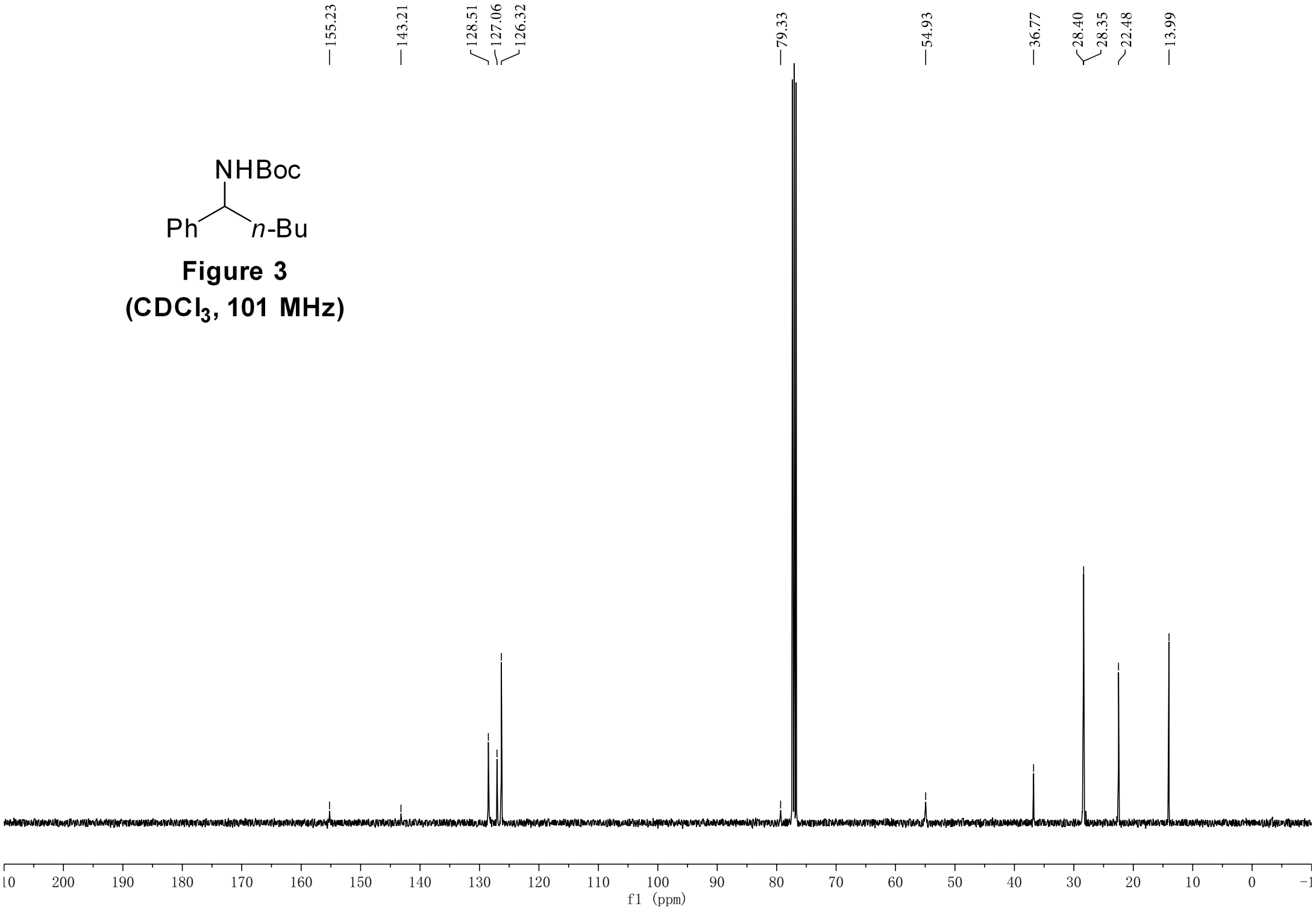



**Figure 3**
**($CDCl_3$, 101 MHz)**

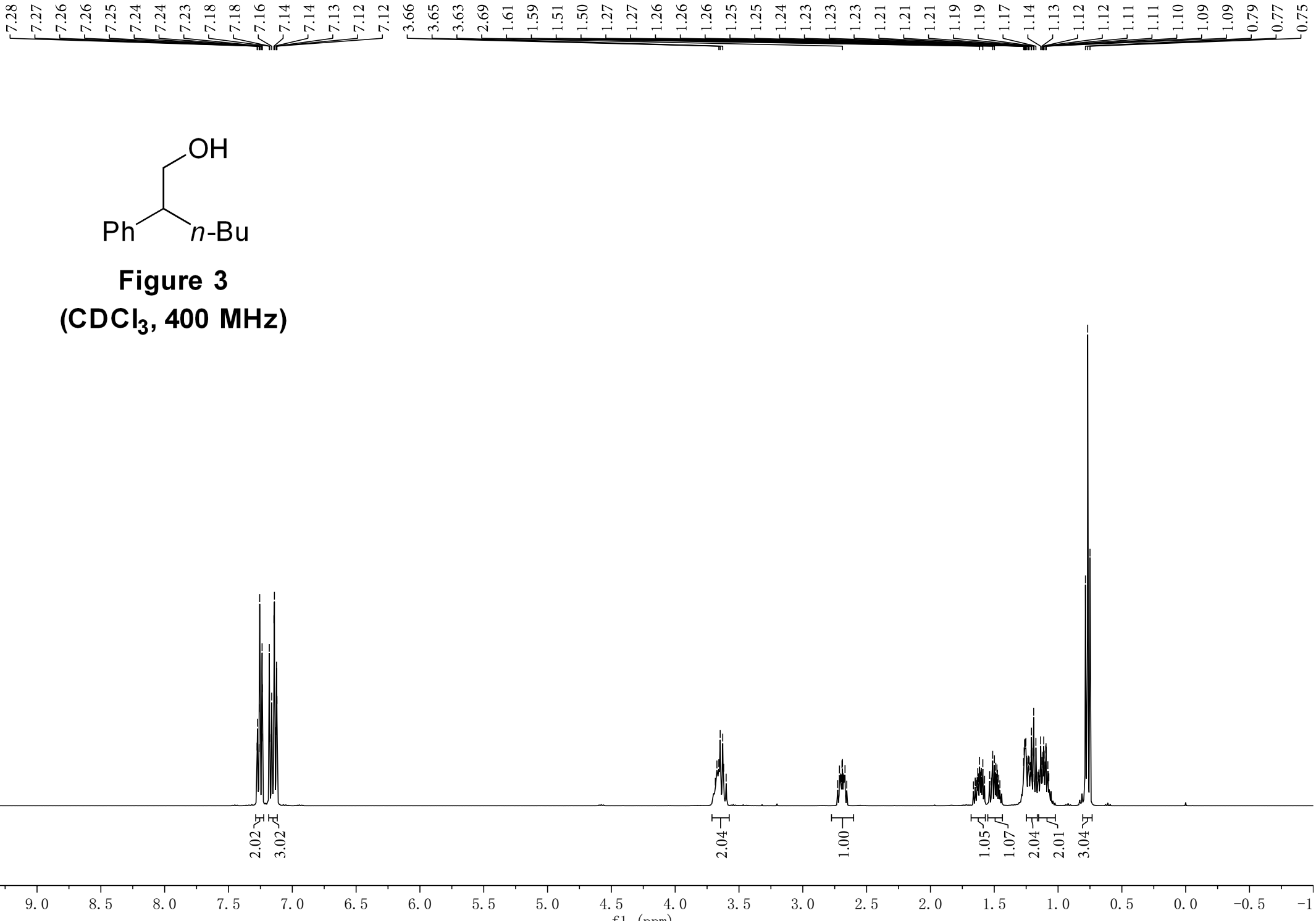



**Figure 3**
**($CDCl_3$, 400 MHz)**

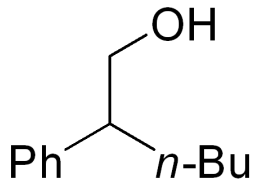



**Figure 3**
**($CDCl_3$, 101 MHz)**

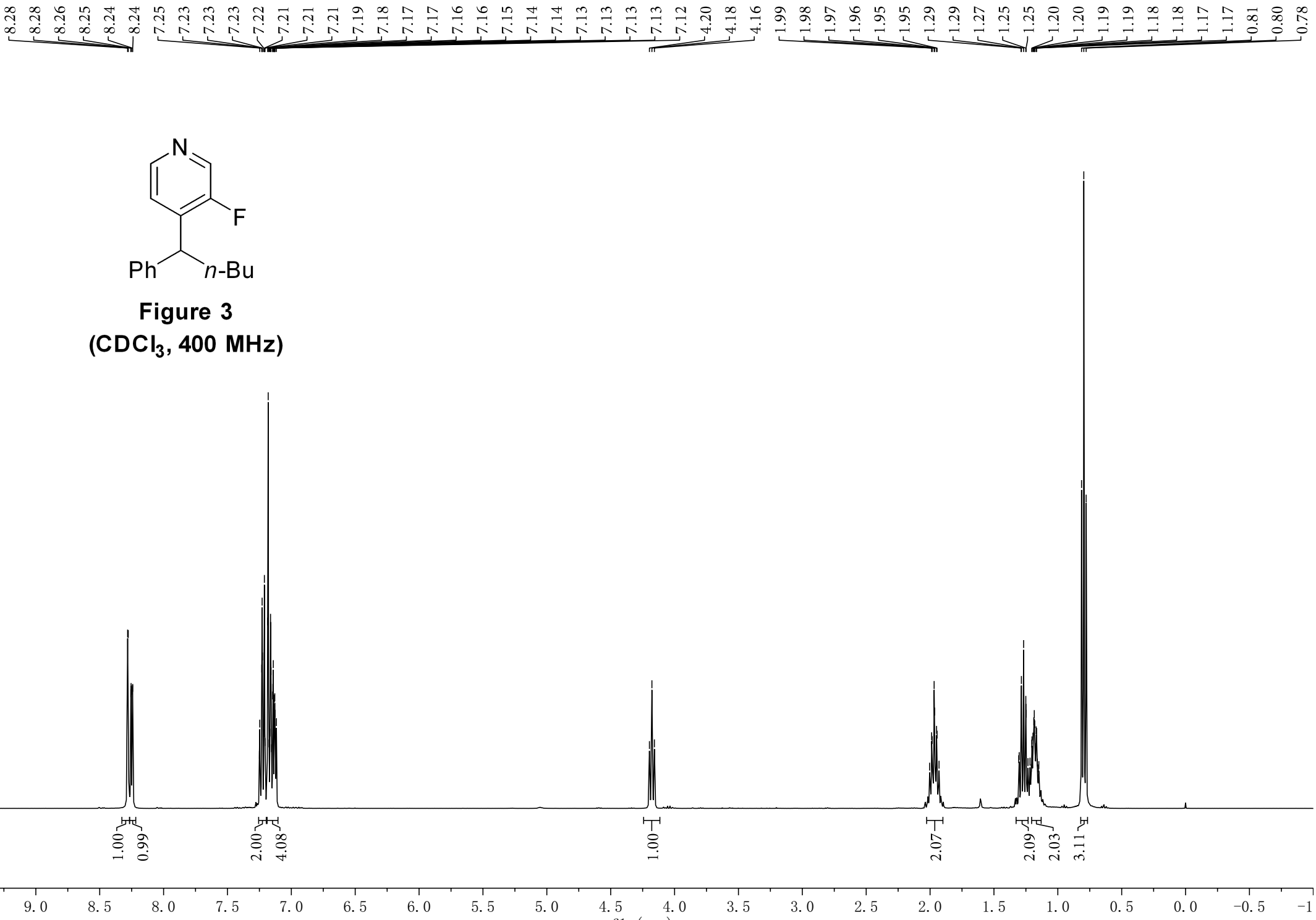



**Figure 3**
**($CDCl_3$, 400 MHz)**

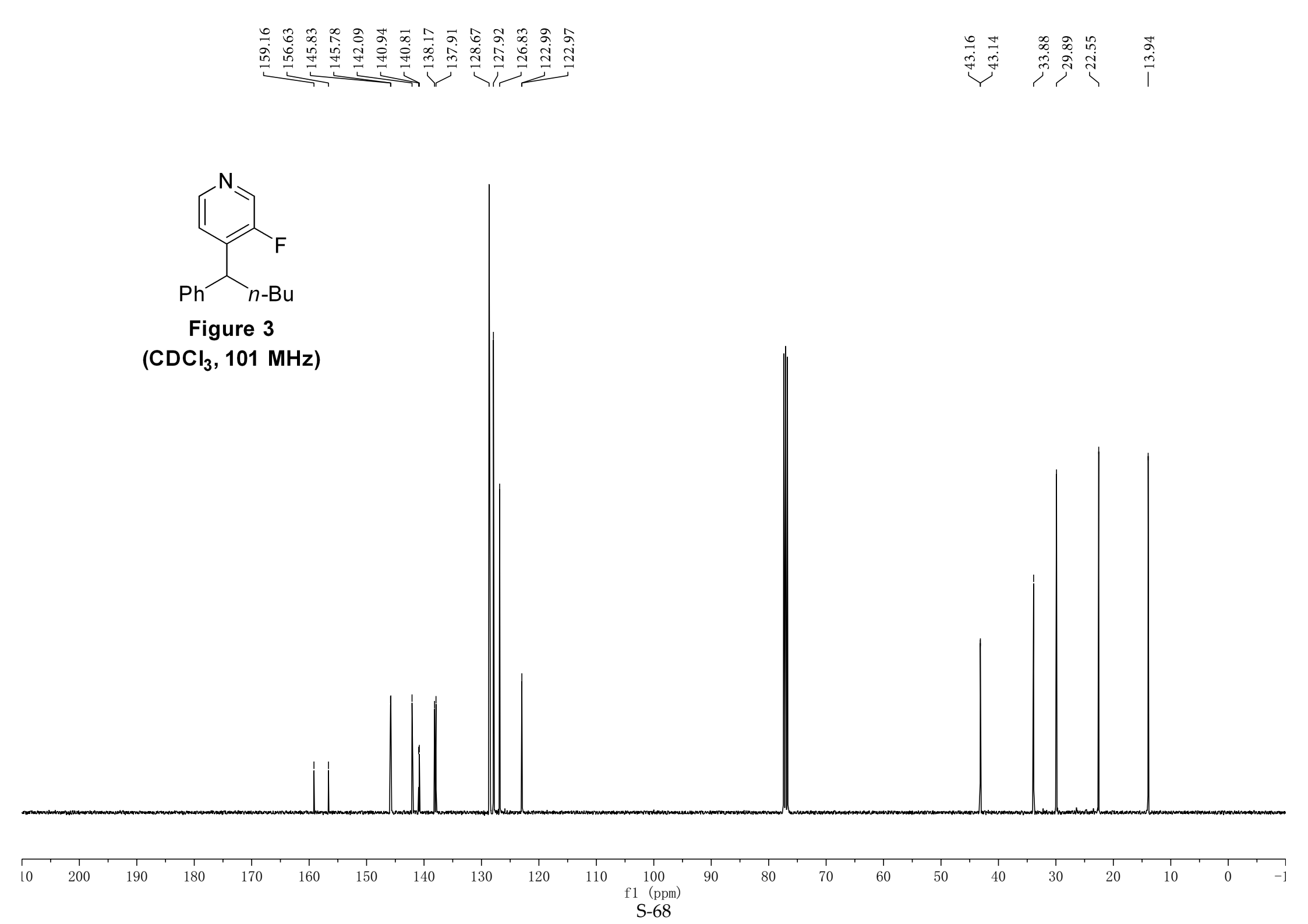



**Figure 3**
**($CDCl_3$, 101 MHz)**

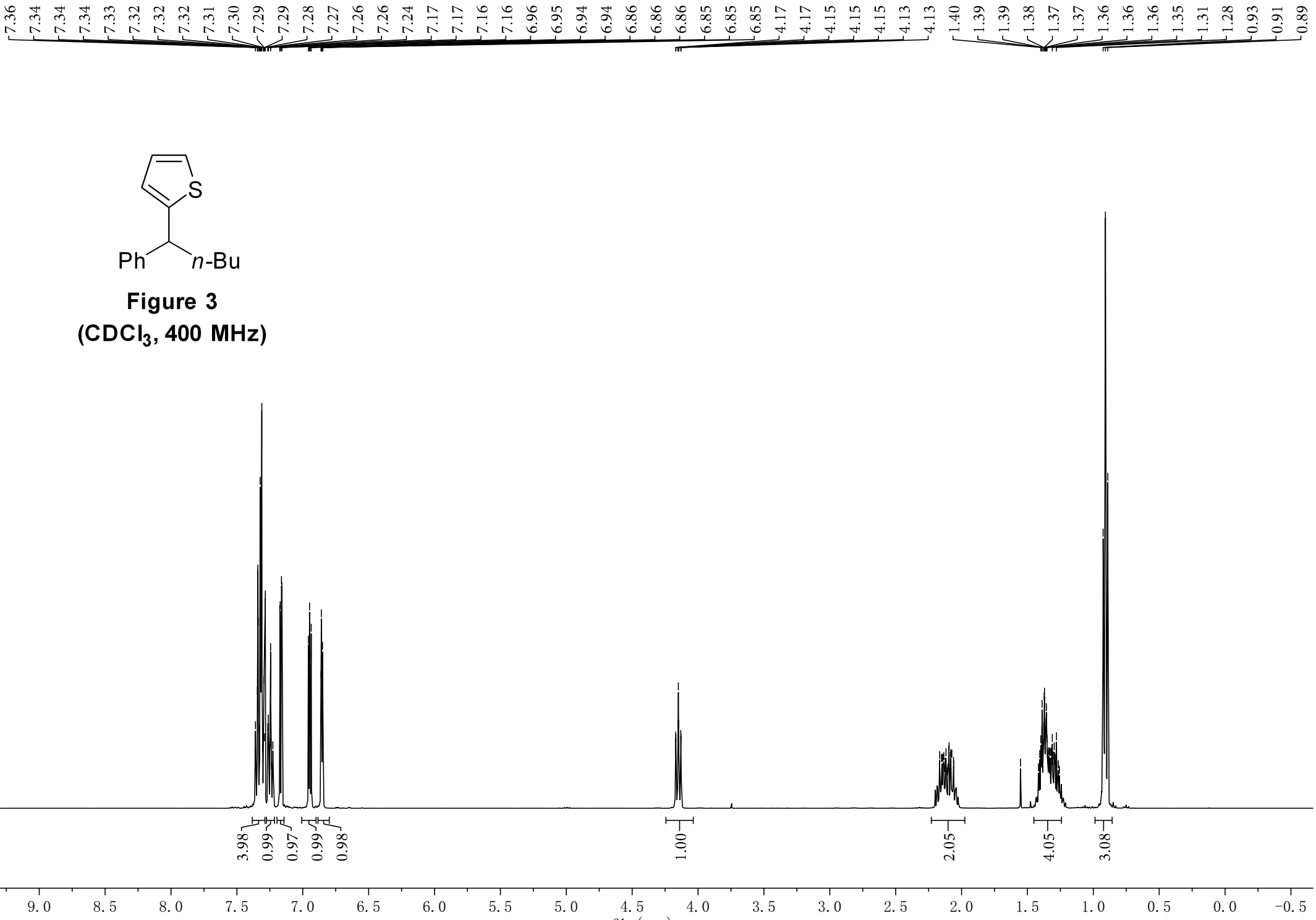



**Figure 3**
**($CDCl_3$, 400 MHz)**

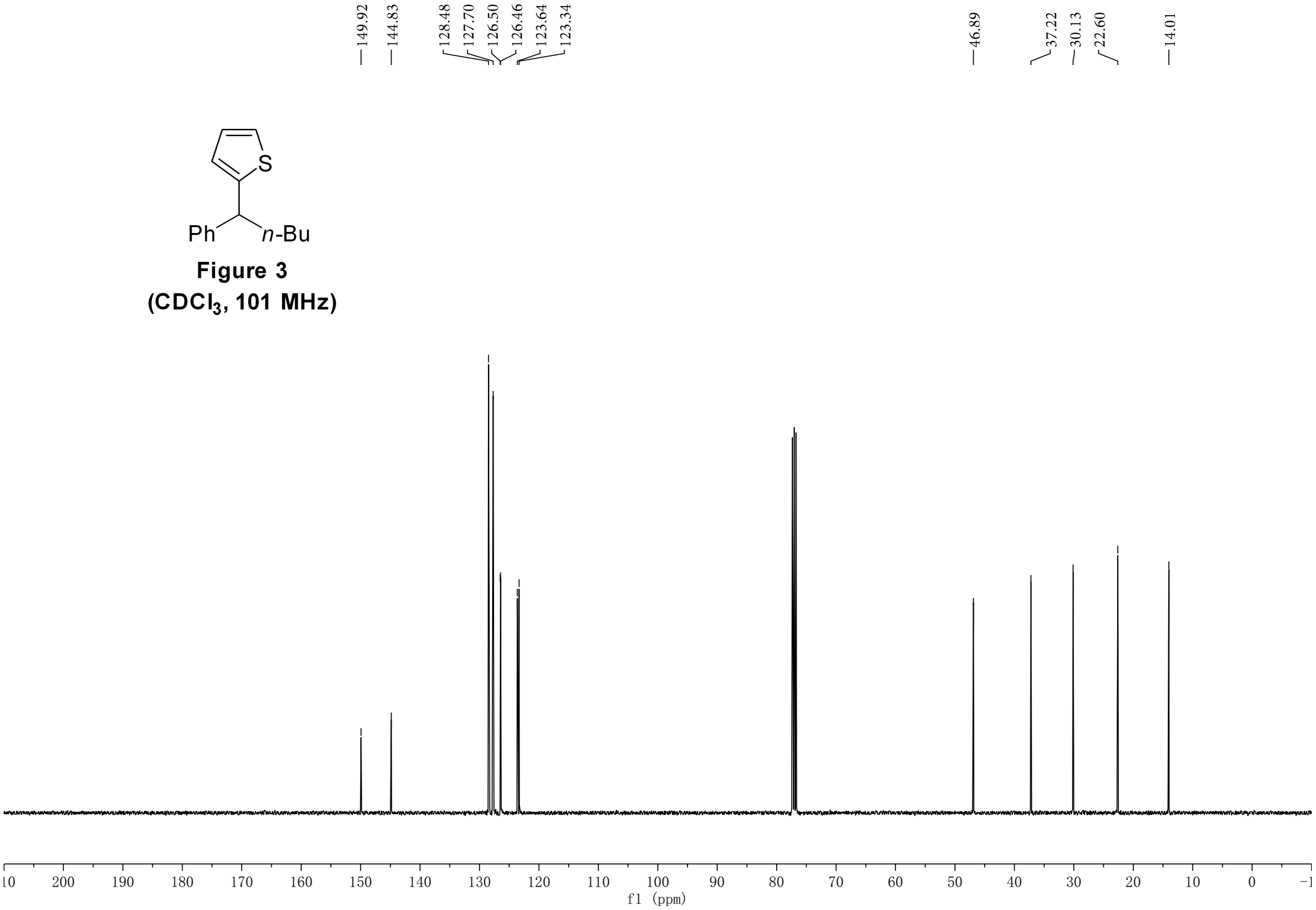
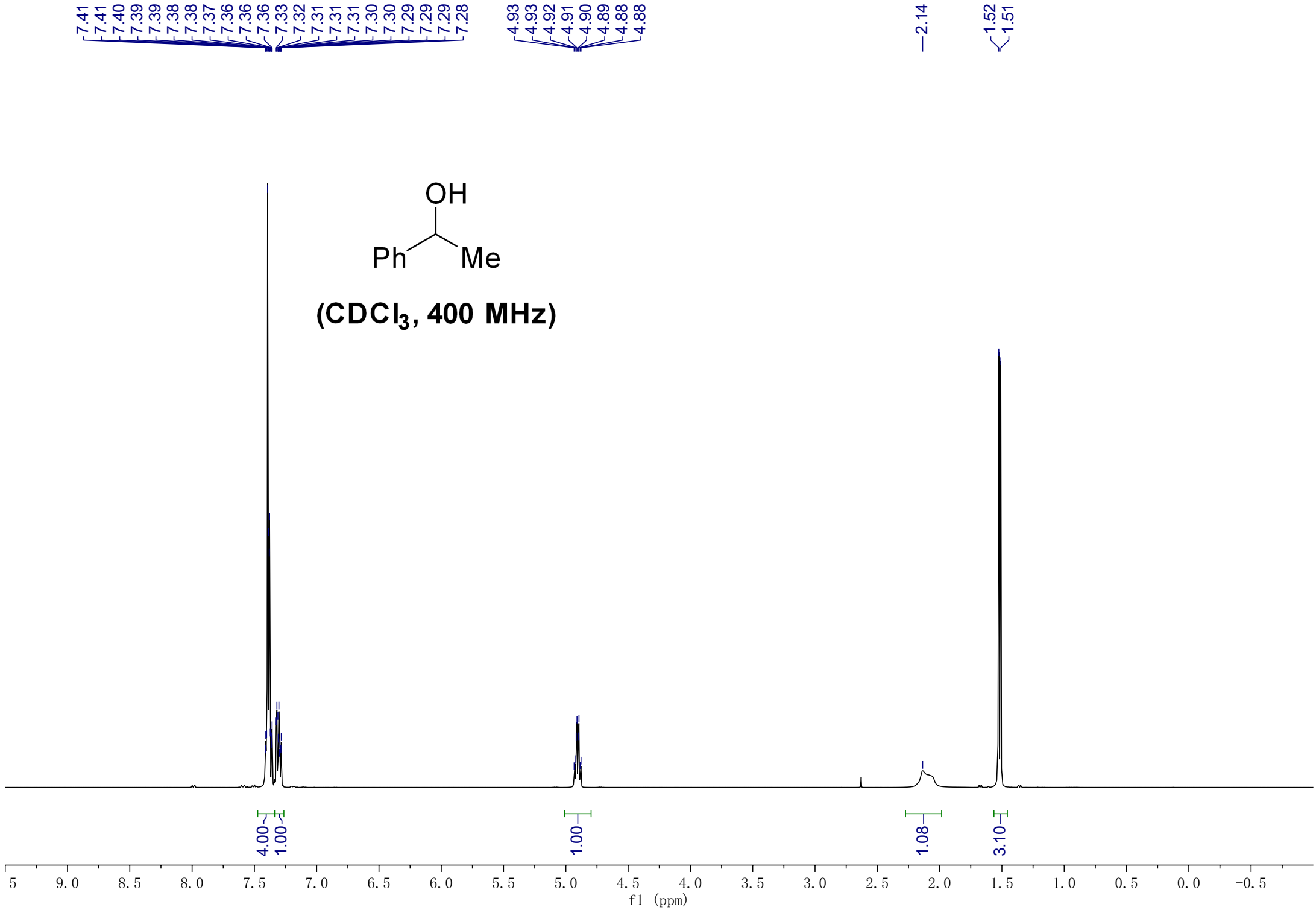
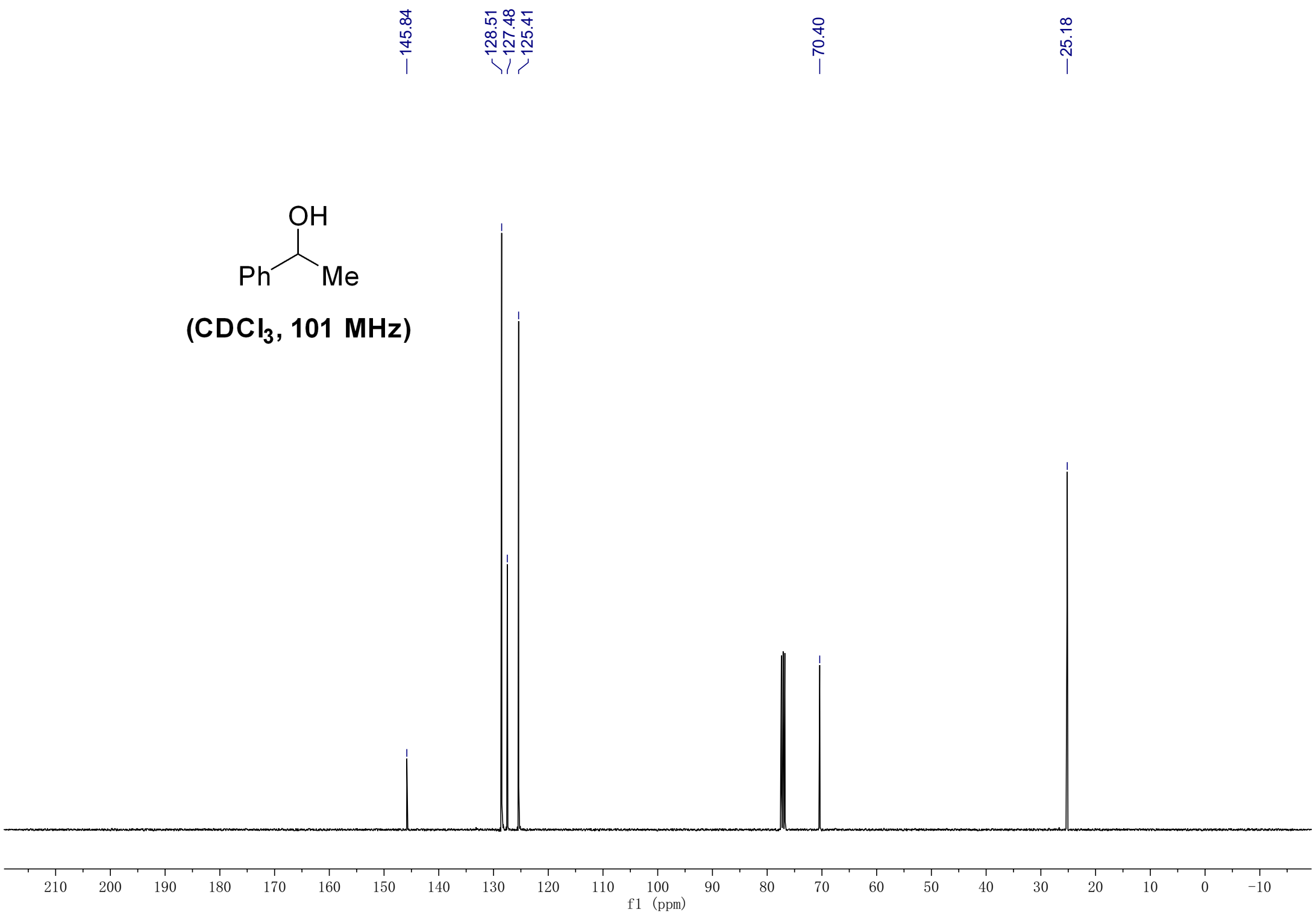
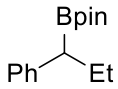



**Figure 3**
**($CDCl_3$, 101 MHz)**

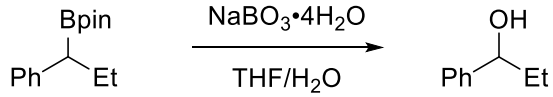

7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
4.93
4.93
4.92
4.91
4.90
4.89
4.88
4.88
2.14
1.52
1.51
OH
Ph
Me
(CDCl3, 400 MHz)
4.00
1.00
1.00
1.08
3.10
f1 (ppm)


145.84
128.51
127.48
125.41
70.40
25.18
OH
Ph
Me
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

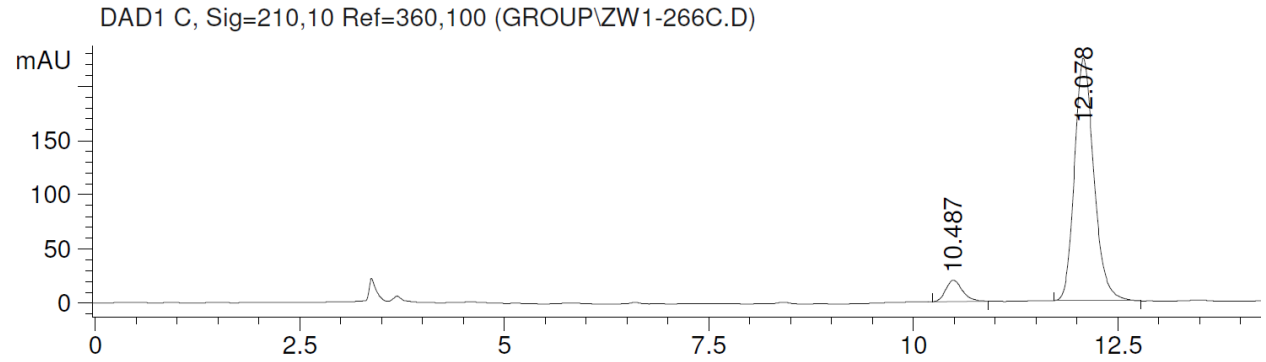
## ee Analysis




**4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (Table 2, entry 1).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

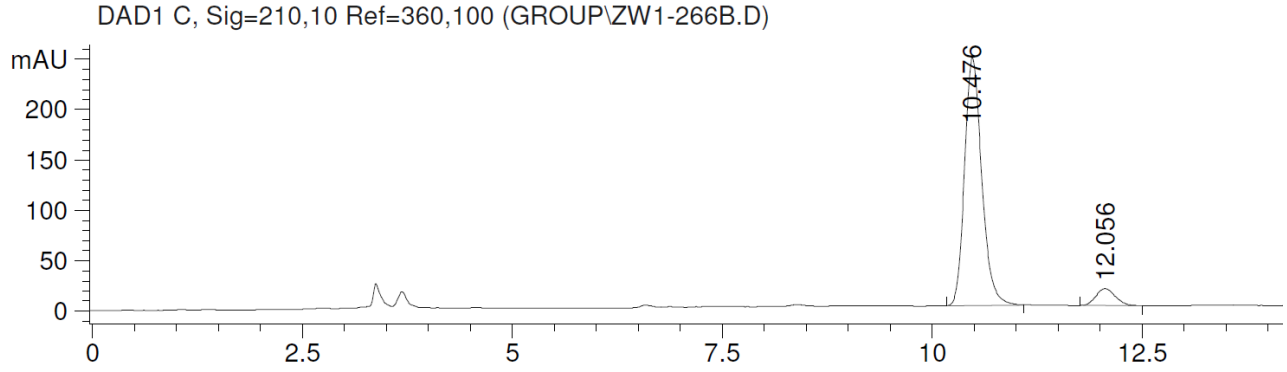



HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).
86% ee from (*R,S*)-**L1**

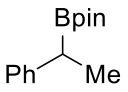



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.487 | BB | 0.2173 | 283.06323 | 19.74220 | 7.1185 |
| 2 | 12.078 | BP | 0.2546 | 3693.40063 | 223.75386 | 92.8815 |

86% ee from (*S,R*)-**L1**

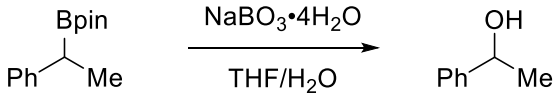



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.476 | BB | 0.2185 | 3511.21704 | 246.06520 | 92.8904 |
| 2 | 12.056 | PP | 0.2419 | 268.73889 | 16.86695 | 7.1096 |



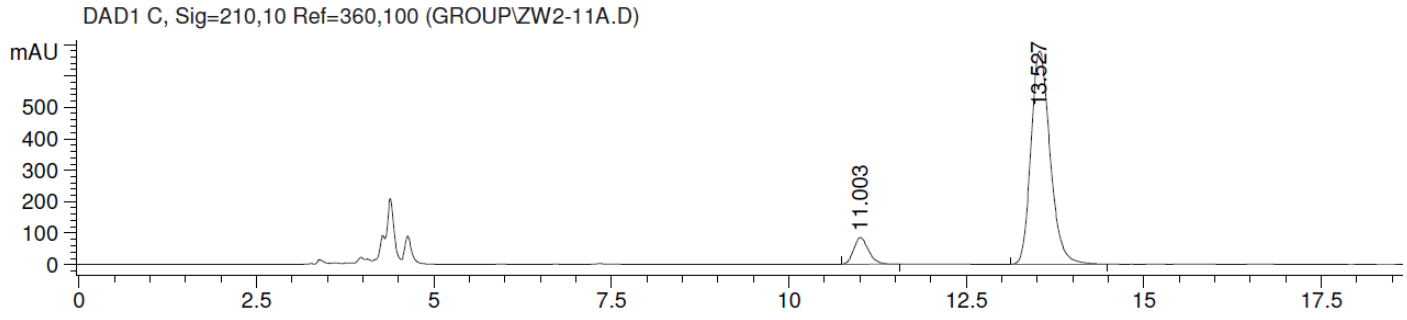

**4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (Table 2, entry 2).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



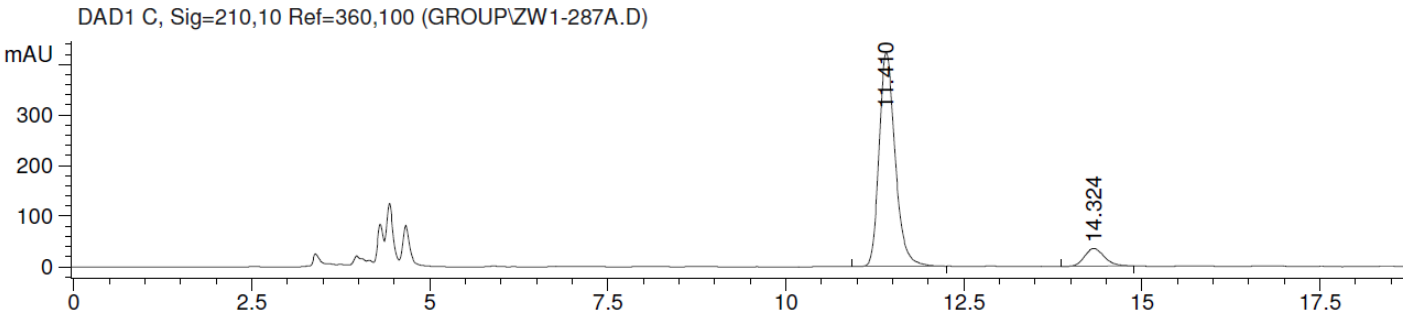

HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

82% ee from (*R,S*)-**L1**

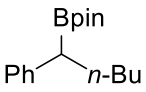



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.003 | BB | 0.2246 | 1233.46497 | 84.34320 | 8.8354 |
| 2 | 13.527 | BB | 0.2906 | 1.27270e4 | 679.18561 | 91.1646 |

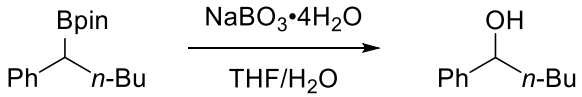
81% ee from (*S,R*)-**L1**



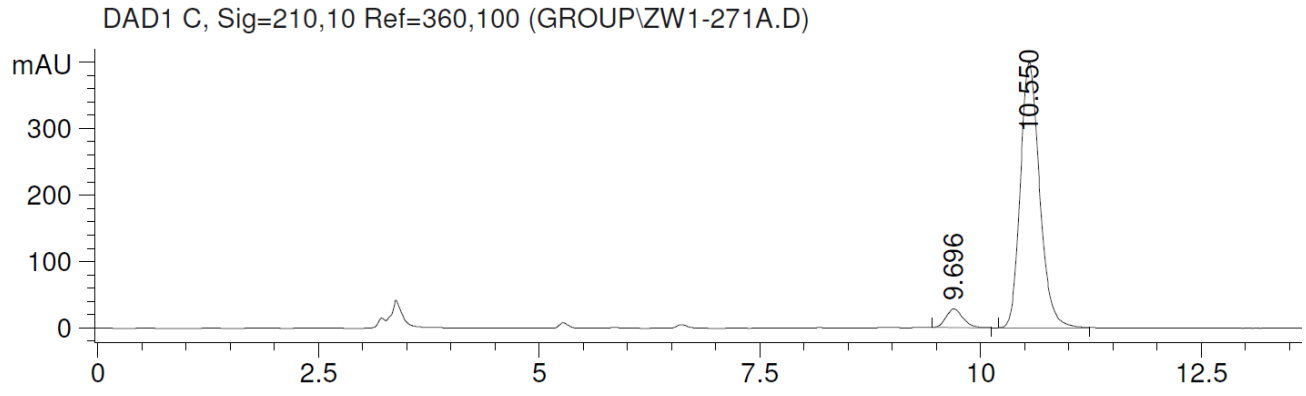

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.410 | PB | 0.2408 | 6616.96777 | 422.26740 | 90.5339 |
| 2 | 14.324 | PB | 0.2980 | 691.86249 | 35.39775 | 9.4661 |




**4,4,5,5-Tetramethyl-2-(1-phenylpentyl)-1,3,2-dioxaborolane (Table 2, entry 3).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

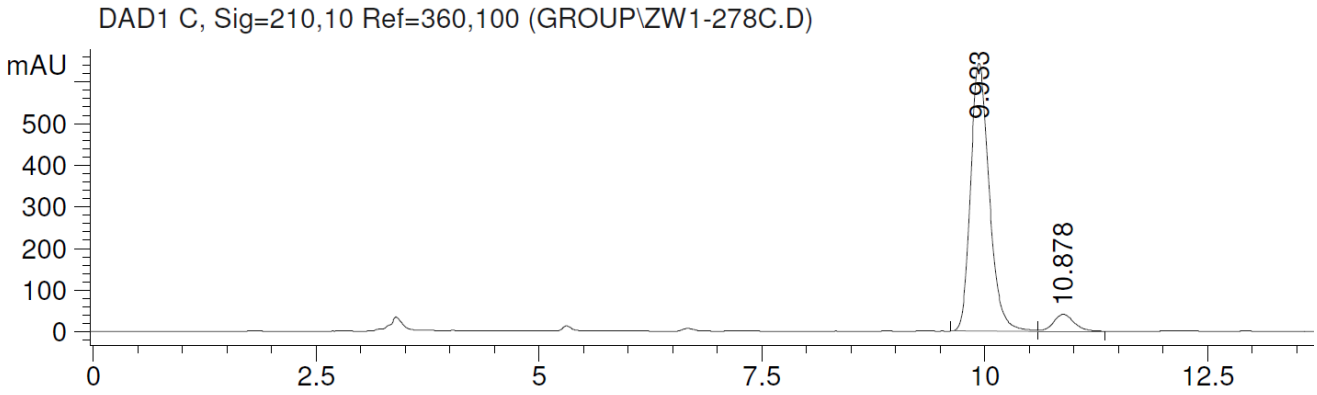



HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).
88% ee from (*R,S*)-**L1**

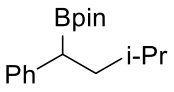



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.696 | BB | 0.2092 | 377.45020 | 28.01860 | 5.8609 |
| 2 | 10.550 | BB | 0.2353 | 6062.72705 | 398.93619 | 94.1391 |

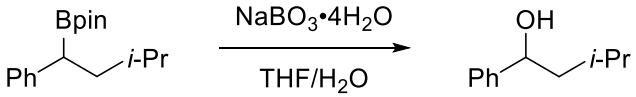
87% ee from (*S,R*)-**L1**



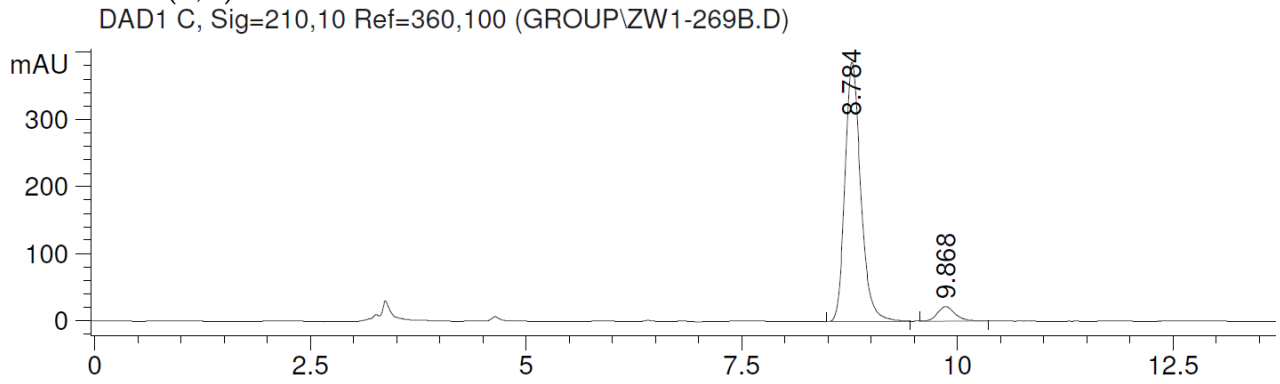

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.933 | BV | 0.2236 | 9368.13574 | 644.53461 | 93.5385 |
| 2 | 10.878 | VB | 0.2429 | 647.13910 | 40.84246 | 6.4615 |




**4,4,5,5-Tetramethyl-2-(3-methyl-1-phenylbutyl)-1,3,2-dioxaborolane (Table 2, entry 4).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

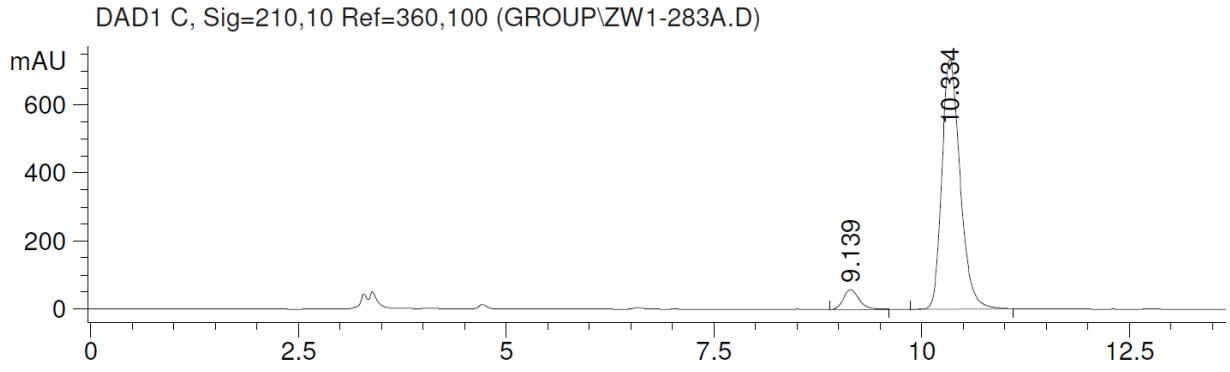



HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).
88% ee from (*R,S*)-**L1**

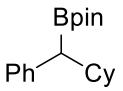



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.784 | PB | 0.1947 | 4919.49951 | 386.00101 | 94.1030 |
| 2 | 9.868 | BB | 0.2184 | 308.28378 | 21.61554 | 5.8970 |

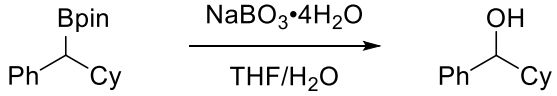
87% ee from (*S,R*)-**L1**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.139 | PB | 0.2000 | 759.79712 | 58.32104 | 6.3311 |
| 2 | 10.334 | PB | 0.2359 | 1.12412e4 | 737.09137 | 93.6689 |

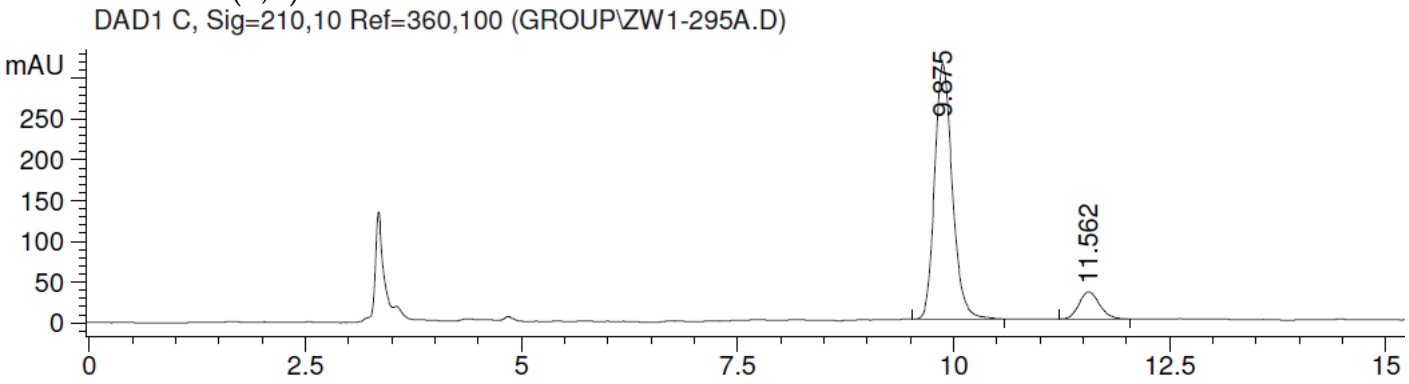



**2-(Cyclohexyl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 5).**
Determination of the ee: stereospecific oxidation according to **GP-3**.



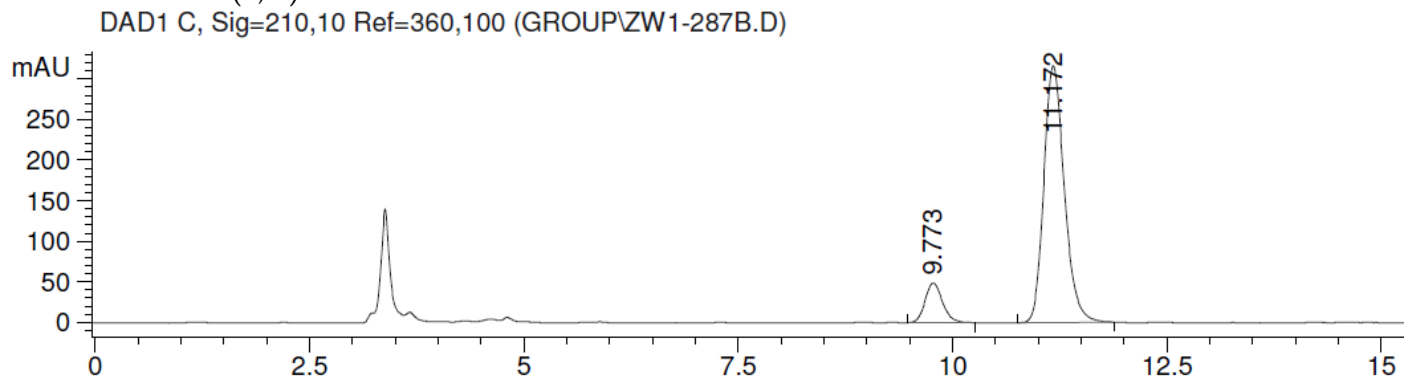

HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

78% ee from (*R*,*S*)-**L1**

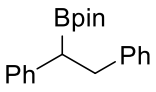



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.875 | BB | 0.2208 | 4499.75146 | 314.70139 | 89.0275 |
| 2 | 11.562 | BB | 0.2552 | 554.58557 | 33.48207 | 10.9725 |

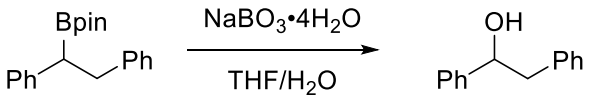
77% ee from (*S*,*R*)-**L1**



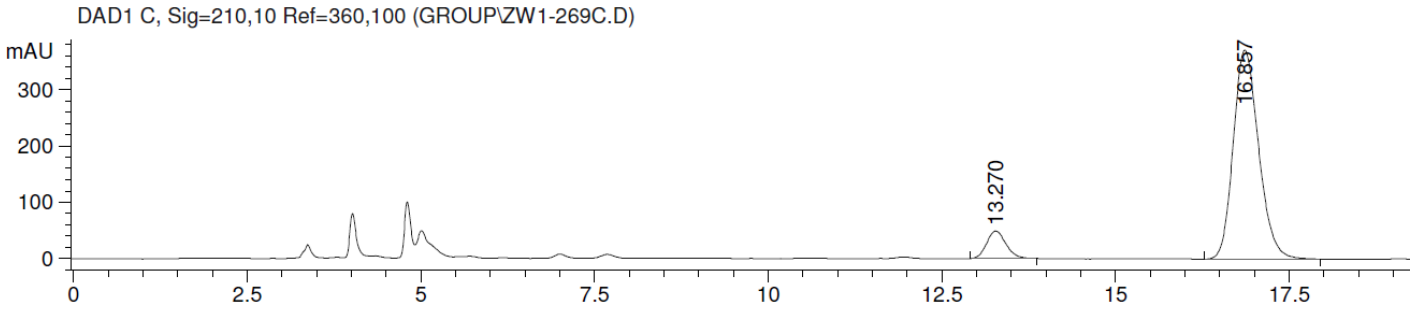

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.773 | BB | 0.2172 | 696.82031 | 49.22257 | 11.6433 |
| 2 | 11.172 | BB | 0.2563 | 5287.89209 | 317.58237 | 88.3567 |




**2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 6).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

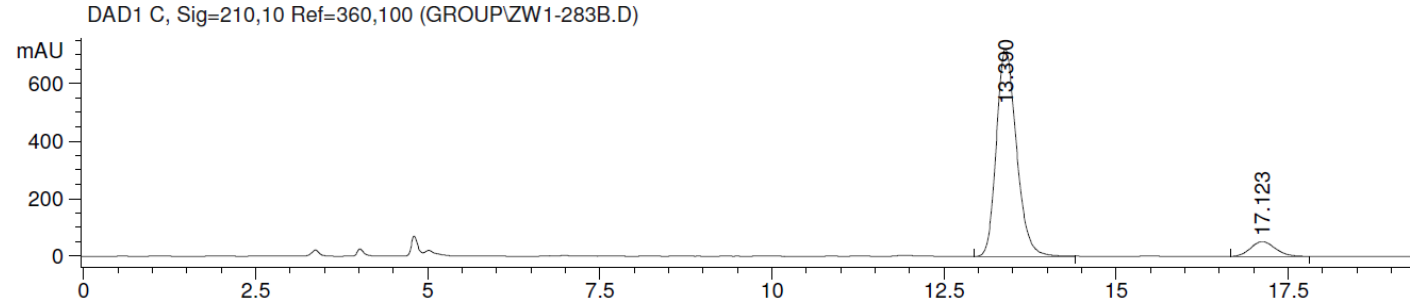



HPLC analysis: CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).
82% ee from (*R,S*)-**L1**

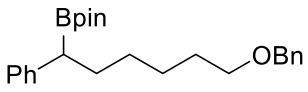



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.270 | BB | 0.3023 | 949.07288 | 48.93923 | 9.1447 |
| 2 | 16.857 | PB | 0.3940 | 9429.27734 | 371.64548 | 90.8553 |

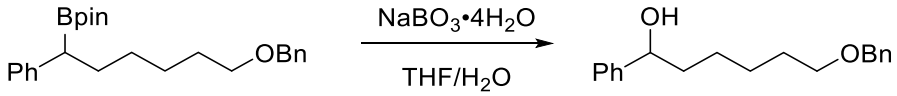
84% ee from (*S,R*)-**L1**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.390 | PB | 0.3120 | 1.45777e4 | 720.69409 | 91.9774 |
| 2 | 17.123 | BB | 0.3746 | 1271.51611 | 51.40392 | 8.0226 |

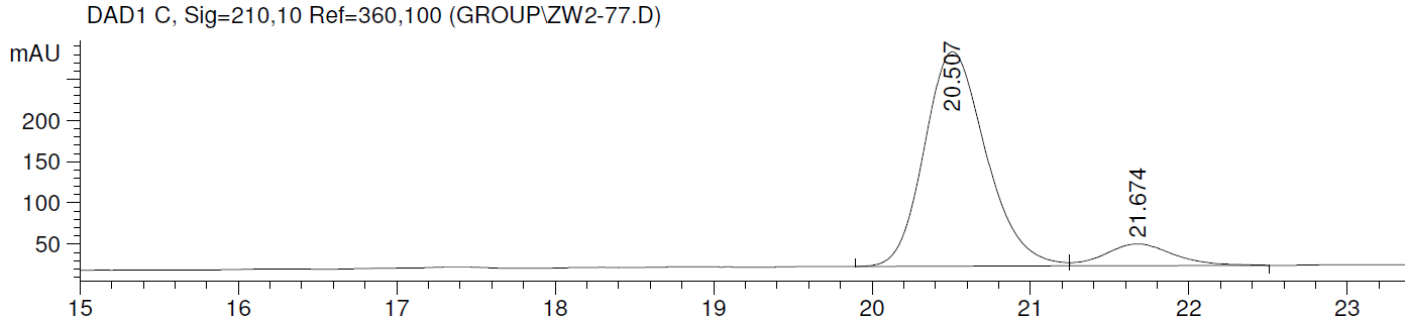



**2-(6-(Benzyloxy)-1-phenylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 7).**
Determination of the ee: stereospecific oxidation according to **GP-3**.



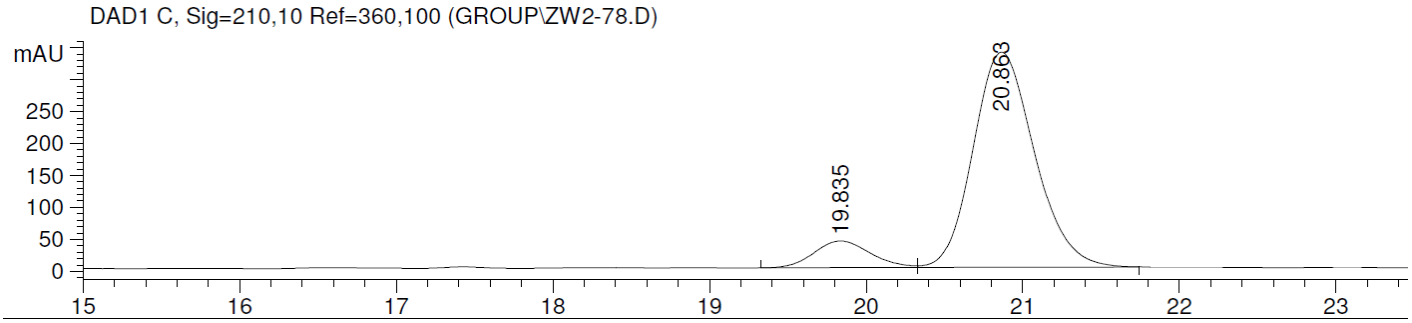

HPLC analysis: CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

80% ee from (*R,S*)-**L1**

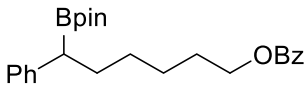



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.507 | BV | 0.4173 | 7032.05615 | 260.22311 | 89.8345 |
| 2 | 21.674 | VB | 0.4312 | 795.73743 | 26.43377 | 10.1655 |

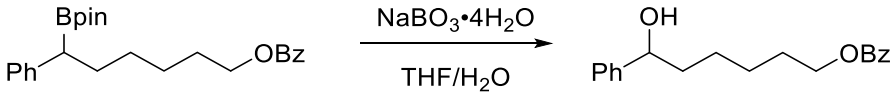
79% ee from (*S,R*)-**L1**



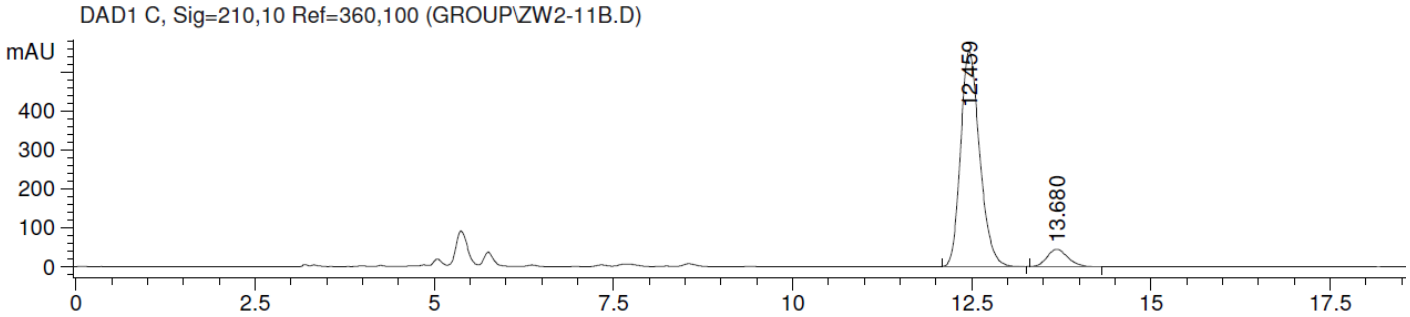

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.835 | BV | 0.3849 | 1052.63672 | 41.92645 | 10.3148 |
| 2 | 20.863 | VB | 0.4209 | 9152.43848 | 336.90317 | 89.6852 |




**6-Phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate (Table 2, entry 8).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

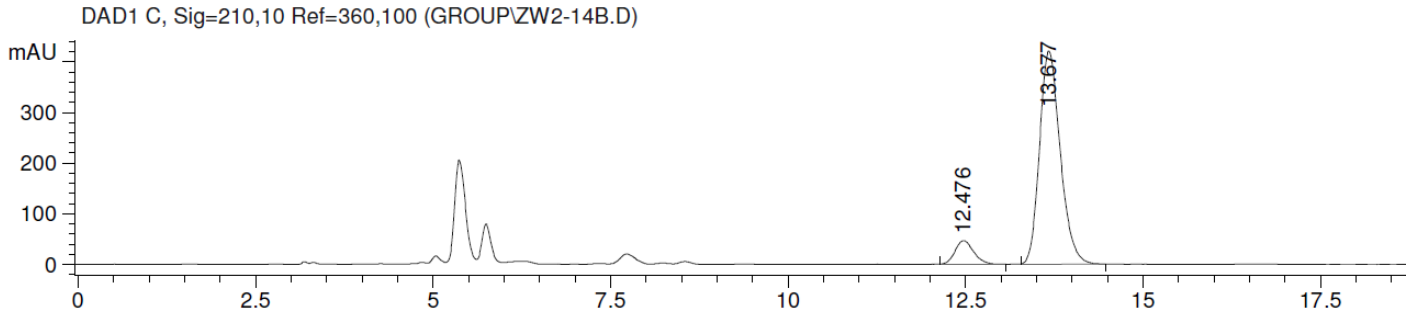



HPLC analysis: CHIRALCEL AD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).
84% ee from (*R,S*)-**L1**

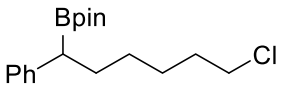



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.459 | BB | 0.2862 | 1.02942e4 | 555.61816 | 91.8048 |
| 2 | 13.680 | BB | 0.3134 | 918.93811 | 45.16085 | 8.1952 |

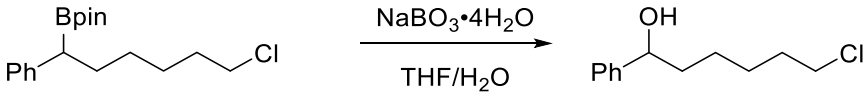
82% ee from (*S,R*)-**L1**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.476 | BB | 0.2822 | 865.63654 | 47.14452 | 9.1816 |
| 2 | 13.677 | BB | 0.3132 | 8562.28320 | 421.18884 | 90.8184 |

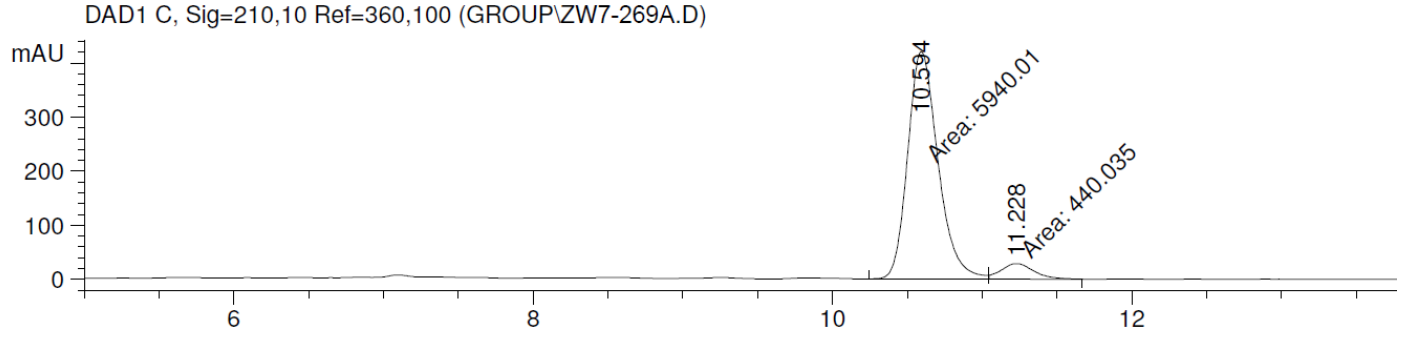



**2-(6-Chloro-1-phenylhexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 9).**
Determination of the ee: stereospecific oxidation according to **GP-3**.



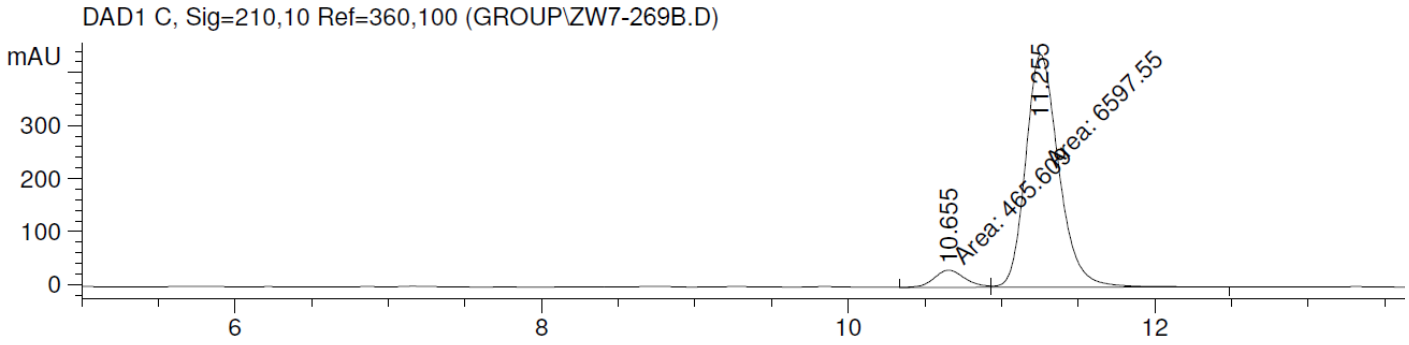

HPLC analysis: CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min).

86% ee from (*R,S*)-**L1**

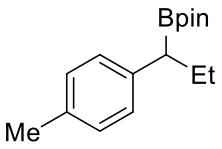



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.594 | MM | 0.2354 | 5940.00537 | 420.53772 | 93.1029 |
| 2 | 11.228 | MM | 0.2542 | 440.03528 | 28.85266 | 6.8971 |

87% ee from (*S,R*)-**L1**

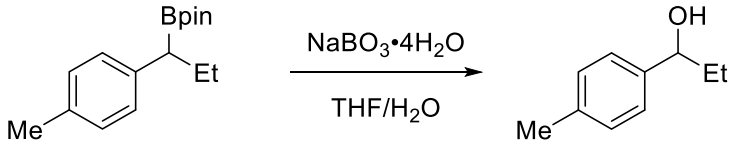



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.655 | MF | 0.2370 | 465.60919 | 32.73672 | 6.5921 |
| 2 | 11.255 | FM | 0.2506 | 6597.55273 | 438.72421 | 93.4079 |



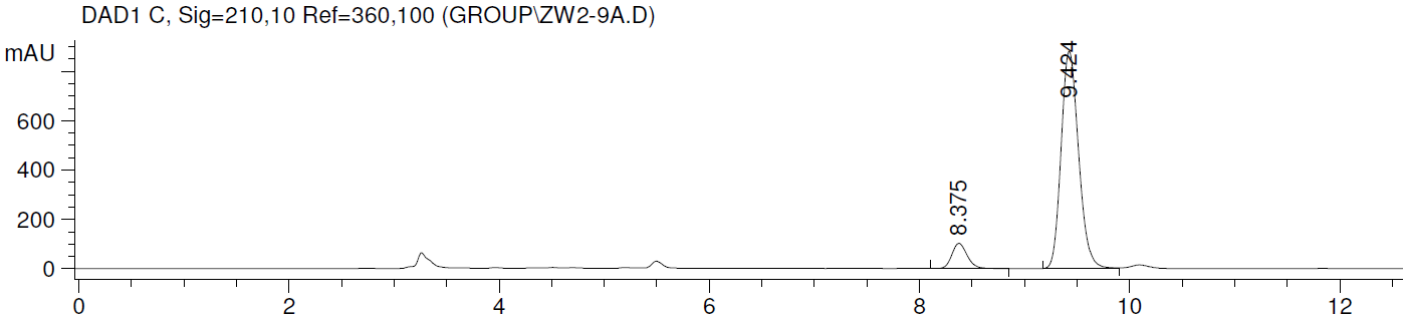

**4,4,5,5-Tetramethyl-2-(1-(p-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, entry 10).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



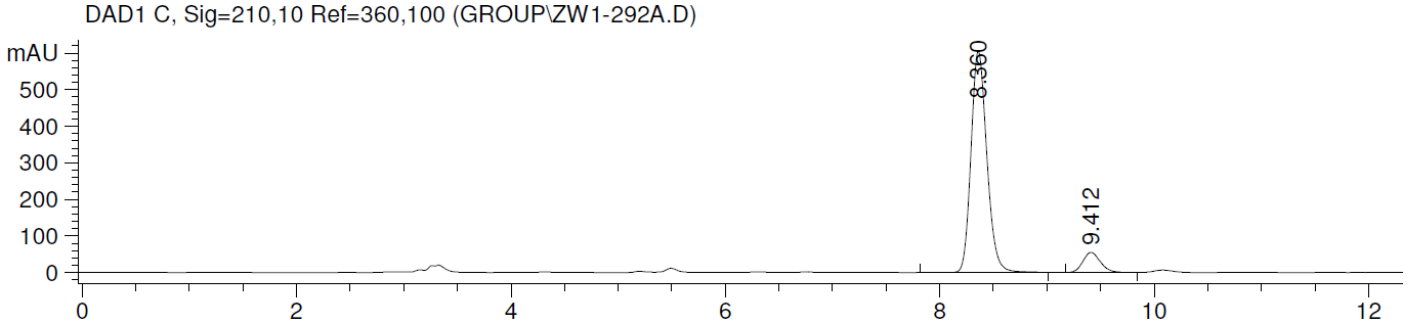

HPLC analysis: CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

82% ee from (*R,S*)-**L1**

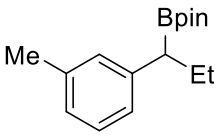



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.375 | VP | 0.1570 | 1044.61426 | 102.42706 | 9.2506 |
| 2 | 9.424 | BV | 0.1815 | 1.02478e4 | 882.18964 | 90.7494 |

82% ee from (*S,R*)-**L1**

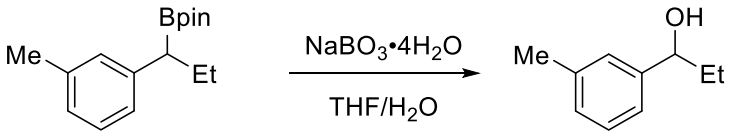



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.360 | PB | 0.1608 | 6269.33740 | 605.38861 | 90.9820 |
| 2 | 9.412 | BP | 0.1757 | 621.40552 | 55.05273 | 9.0180 |



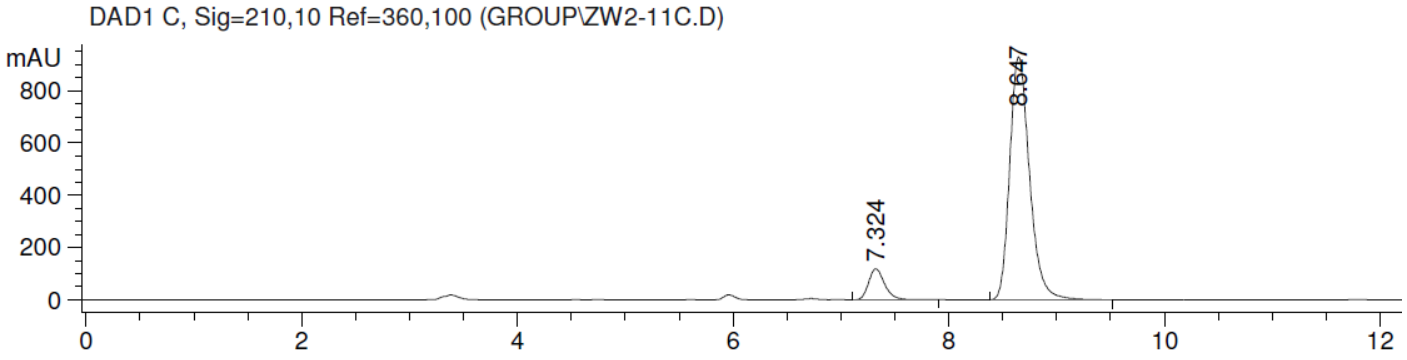

**4,4,5,5-Tetramethyl-2-(1-(m-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, entry 11).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



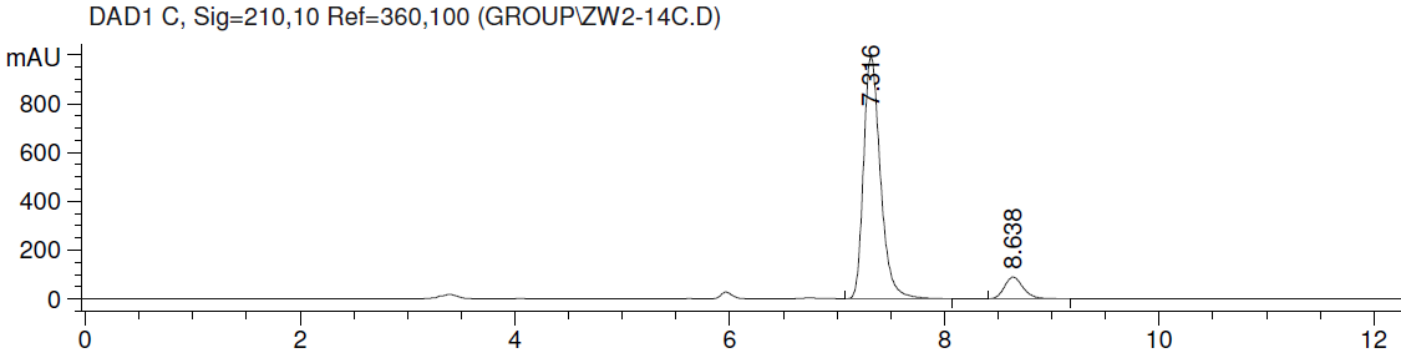

HPLC analysis: CHIRALCEL OD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

81% ee from (*R,S*)-**L1**

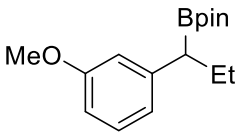



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.324 | VB | 0.1607 | 1254.96533 | 119.32001 | 9.5287 |
| 2 | 8.647 | PP | 0.1994 | 1.19154e4 | 930.35571 | 90.4713 |

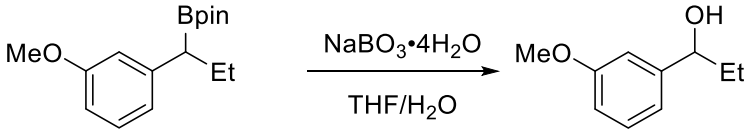
82% ee from (*S,R*)-**L1**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.316 | VB | 0.1695 | 1.08555e4 | 993.59595 | 90.7818 |
| 2 | 8.638 | BB | 0.1899 | 1102.30054 | 89.38408 | 9.2182 |

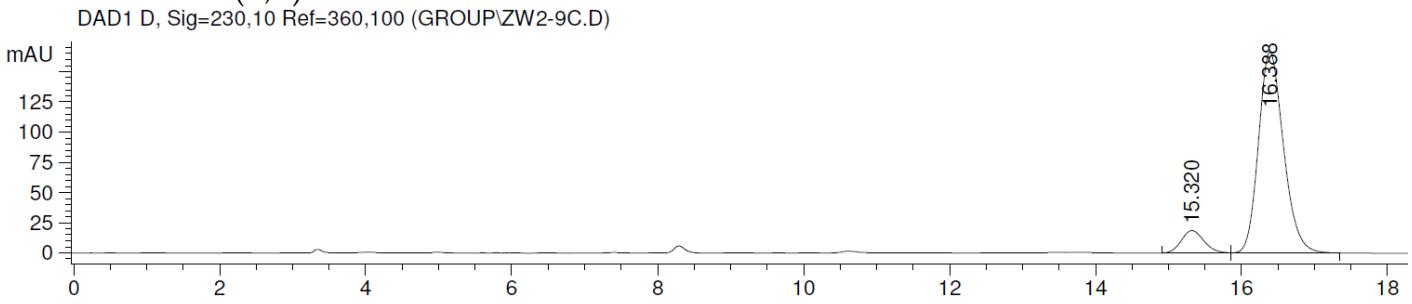



**2-(1-(3-Methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 12).**
Determination of the ee: stereospecific oxidation according to **GP-3**.



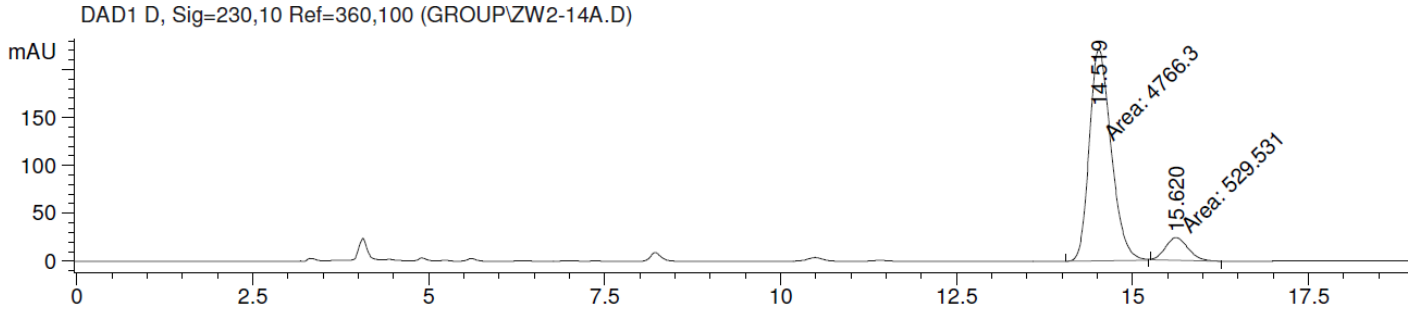

HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

82% ee from (*R,S*)-**L1**

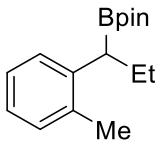



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.320 | BV | 0.3378 | 404.94962 | 18.61724 | 9.2478 |
| 2 | 16.388 | VB | 0.3686 | 3973.94873 | 166.43517 | 90.7522 |

80% ee from (*S,R*)-**L1**

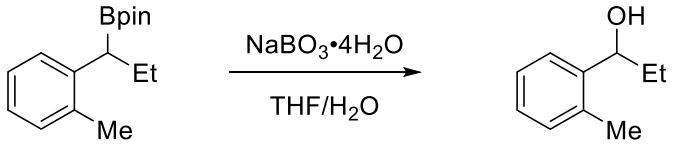



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.519 | MM | 0.3606 | 4766.29980 | 220.30853 | 90.0010 |
| 2 | 15.620 | MM | 0.3731 | 529.53070 | 23.65677 | 9.9990 |



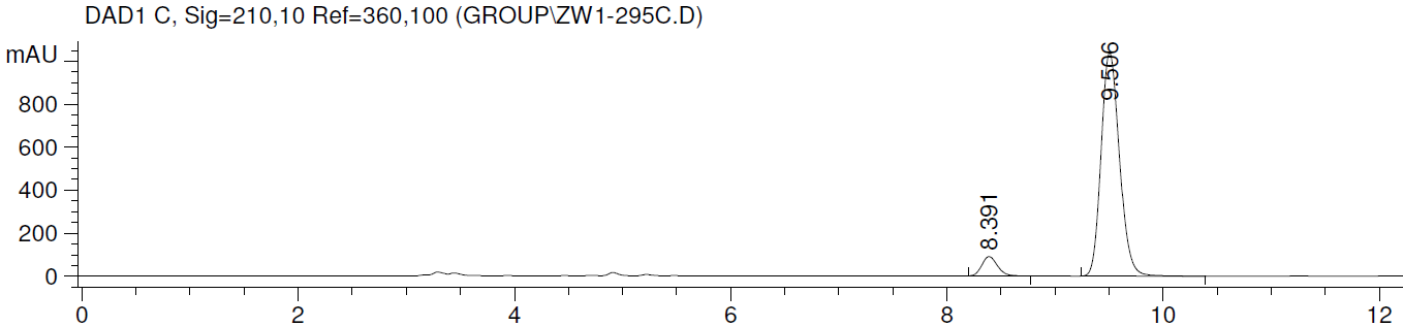

**4,4,5,5-Tetramethyl-2-(1-(o-tolyl)propyl)-1,3,2-dioxaborolane (Table 2, entry 13).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



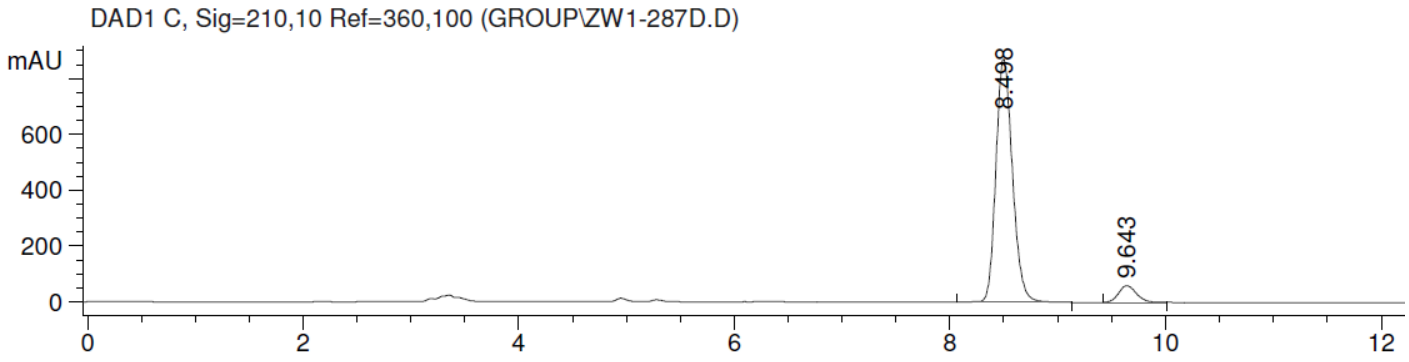

HPLC analysis: CHIRALCEL AD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).

86% ee from (*R,S*)-**L1**

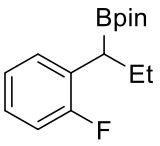



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.391 | BB | 0.1580 | 913.89642 | 90.39434 | 6.9113 |
| 2 | 9.506 | BP | 0.1841 | 1.23094e4 | 1039.77502 | 93.0887 |

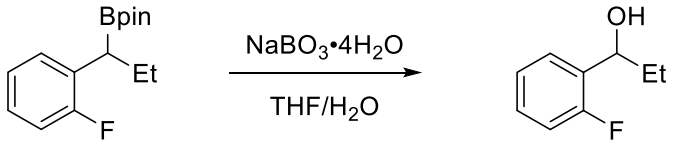
86% ee from (*S,R*)-**L1**



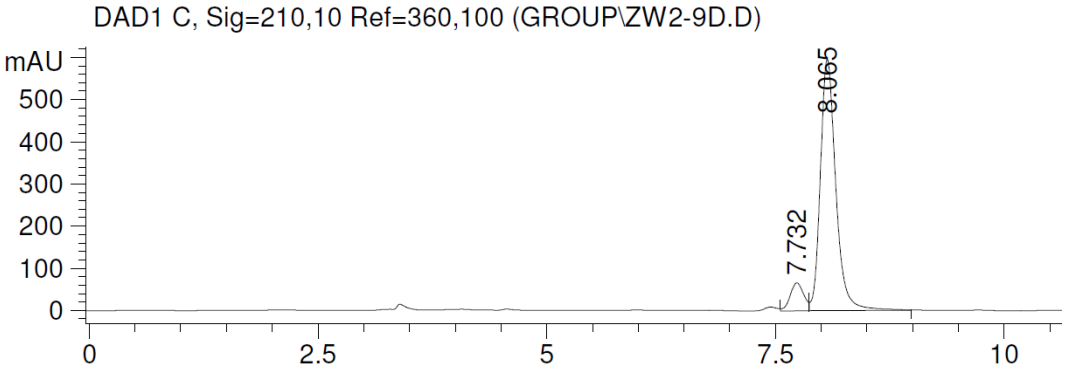

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.498 | BP | 0.1662 | 9274.53809 | 871.08533 | 93.0220 |
| 2 | 9.643 | BB | 0.1767 | 695.72894 | 60.26936 | 6.9780 |




**2-(1-(2-Fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 14).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

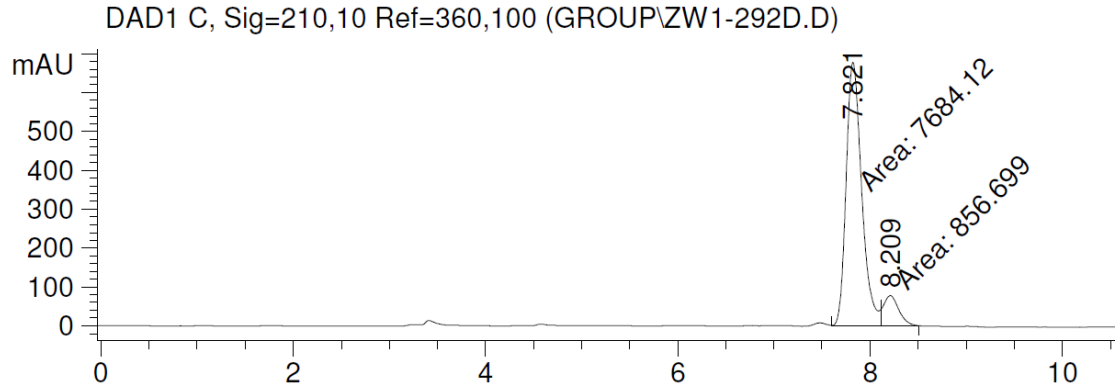



HPLC analysis: CHIRALCEL OD-H column (3% *i*-PrOH in hexane, 1.0 mL/min).
82% ee from (*R,S*)-**L1**

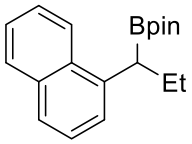



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.732 | VV | 0.1574 | 682.10138 | 66.65819 | 8.8762 |
| 2 | 8.065 | VB | 0.1789 | 7002.49707 | 596.73645 | 91.1238 |

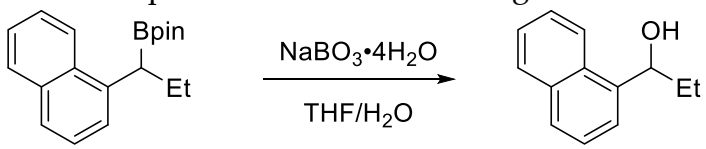
80% ee from (*S,R*)-**L1**



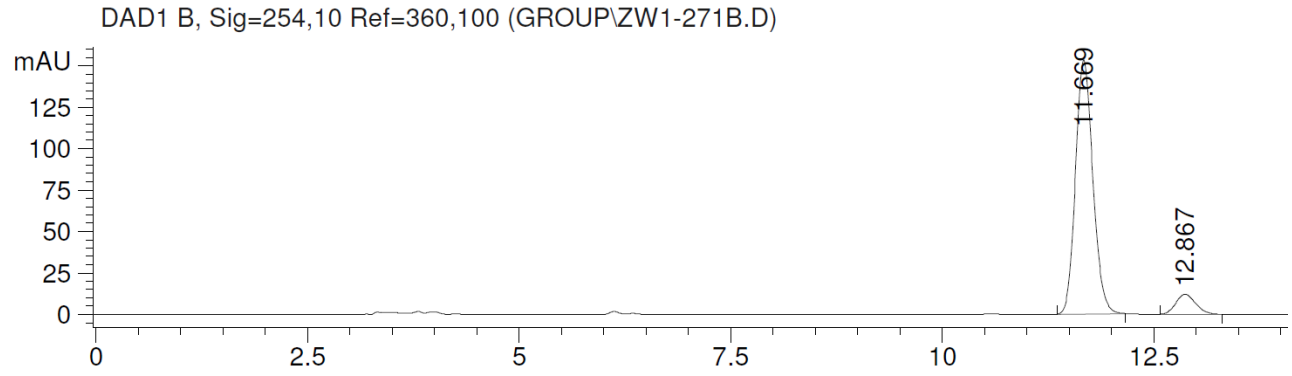

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.821 | MM | 0.1885 | 7684.12109 | 679.34735 | 89.9694 |
| 2 | 8.209 | MM | 0.1828 | 856.69946 | 78.09657 | 10.0306 |




**4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)propyl)-1,3,2-dioxaborolane (Table 2, entry 15).**
Determination of the ee: stereospecific oxidation according to **GP-3**.

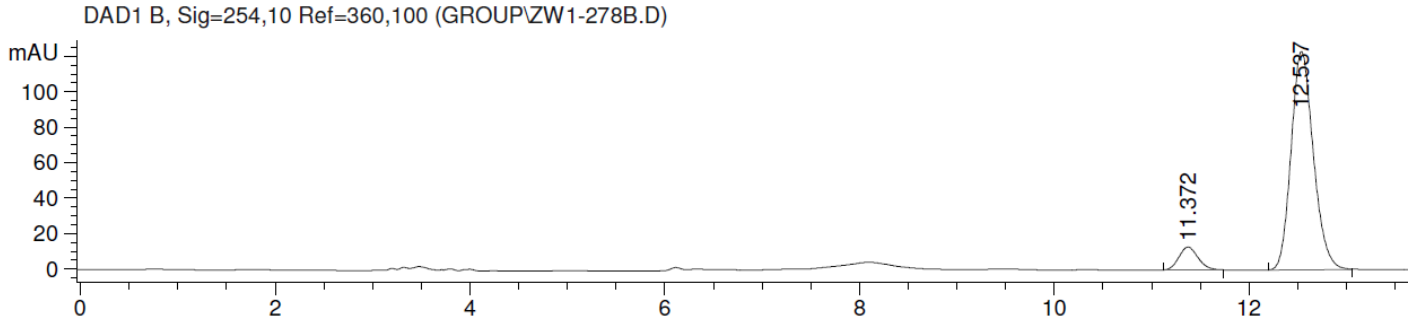



HPLC analysis: CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).
84% ee from (*R,S*)-**L1**

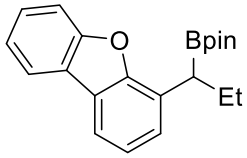



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.669 | BB | 0.2210 | 2201.07544 | 153.80849 | 91.7680 |
| 2 | 12.867 | BB | 0.2505 | 197.44580 | 12.09424 | 8.2320 |

83% ee from (*S,R*)-**L1**

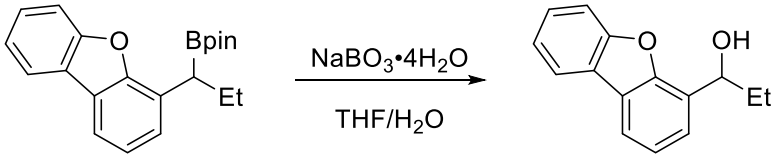



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.372 | BB | 0.2133 | 179.41362 | 12.97424 | 8.4230 |
| 2 | 12.537 | BB | 0.2450 | 1950.63562 | 123.03730 | 91.5770 |



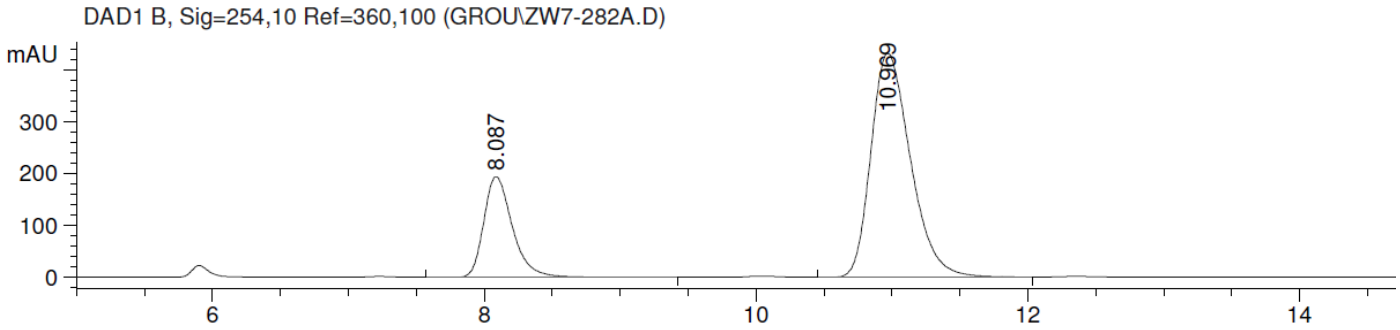

**2-(1-(Dibenzo[*b*,*d*]furan-4-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 16).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



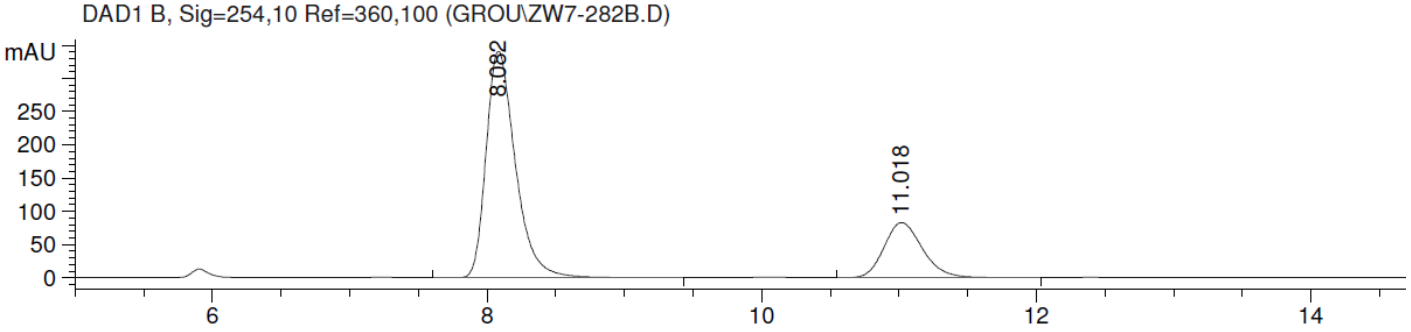

HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

51% ee from (*R*,*S*)-**L1**

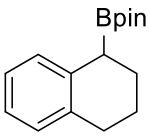



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.087 | VB | 0.2279 | 2869.57080 | 194.80847 | 24.5847 |
| 2 | 10.969 | VV | 0.3133 | 8802.58984 | 432.75644 | 75.4153 |

51% ee from (*S*,*R*)-**L1**

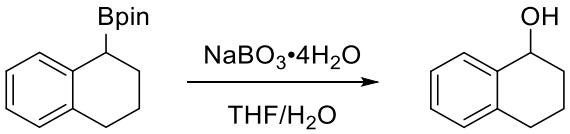



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.082 | VV | 0.2253 | 5065.49951 | 340.98077 | 75.5839 |
| 2 | 11.018 | VV | 0.3021 | 1636.32178 | 82.97614 | 24.4161 |



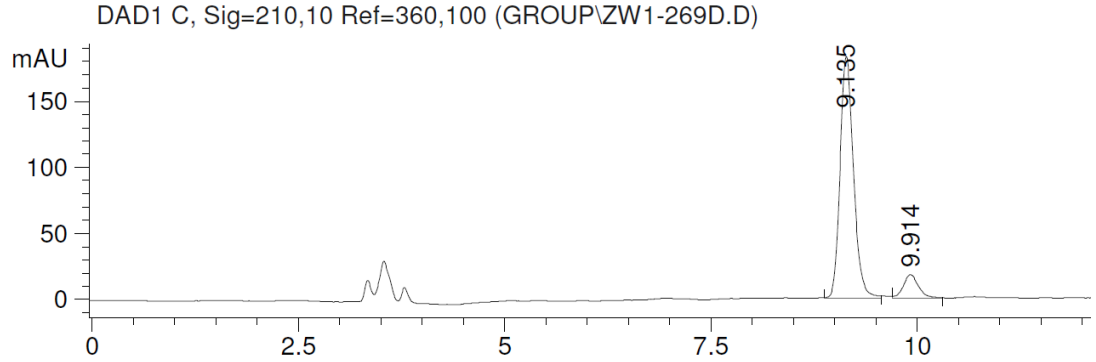

**4,4,5,5-Tetramethyl-2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,3,2-dioxaborolane (Table 2, entry 17).**

Determination of the ee: stereospecific oxidation according to **GP-3**.



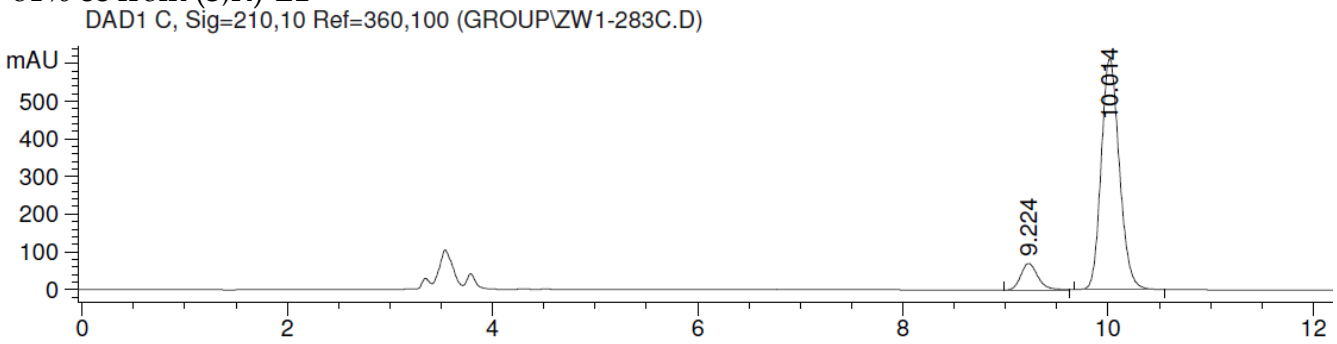

HPLC analysis: CHIRALCEL AD-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

81% ee from (*R,S*)-**L1**

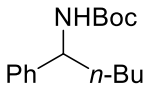



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.135 | BB | 0.1759 | 2066.49219 | 182.74280 | 90.2430 |
| 2 | 9.914 | BB | 0.1902 | 223.42699 | 17.58484 | 9.7570 |

81% ee from (*S,R*)-**L1**



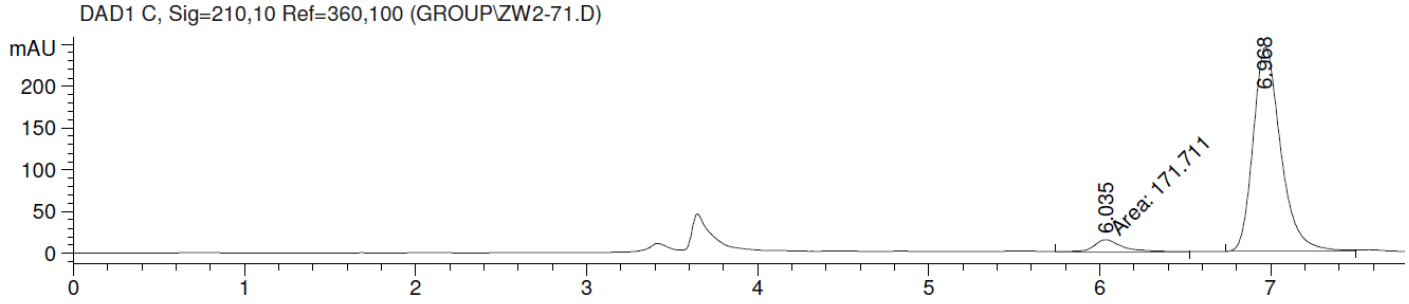

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.224 | PB | 0.1759 | 804.95264 | 70.12235 | 9.6696 |
| 2 | 10.014 | BP | 0.1889 | 7519.61328 | 613.75507 | 90.3304 |




***tert*-Butyl (1-phenylpentyl)carbamate (Fig. 3).**

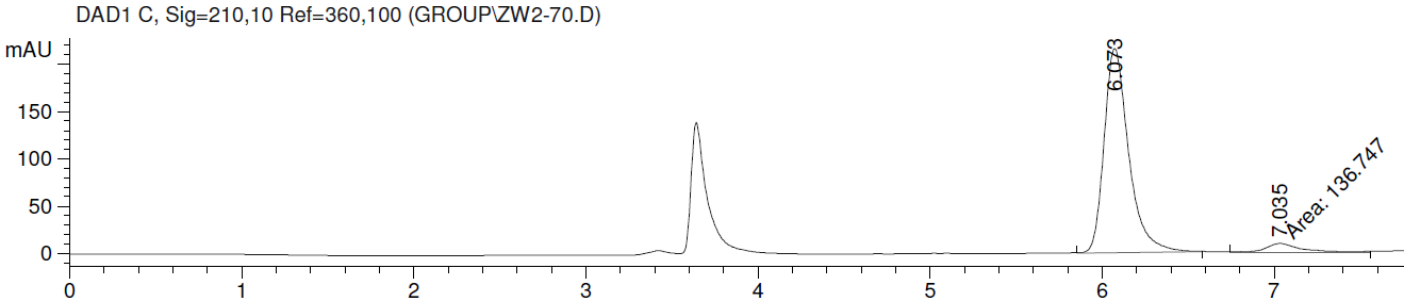
HPLC analysis: CHIRALPAK IC column (3% *i*-PrOH in hexane, 1.0 mL/min).

88% ee from (*R,S*)-**L1**

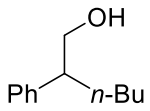



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.035 | MM | 0.1954 | 171.71063 | 14.64886 | 5.8973 |
| 2 | 6.968 | PB | 0.1708 | 2739.96851 | 244.40541 | 94.1027 |

88% ee from (*S,R*)-**L1**



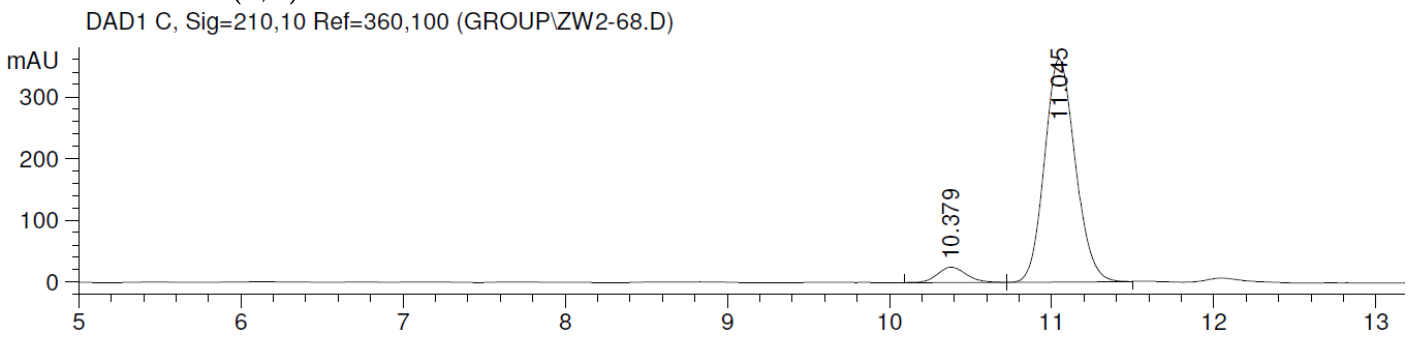

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.073 | BB | 0.1499 | 2144.96313 | 215.85838 | 94.0068 |
| 2 | 7.035 | MM | 0.2455 | 136.74661 | 9.28359 | 5.9932 |




**2-Phenylhexan-1-ol (Fig. 3).**

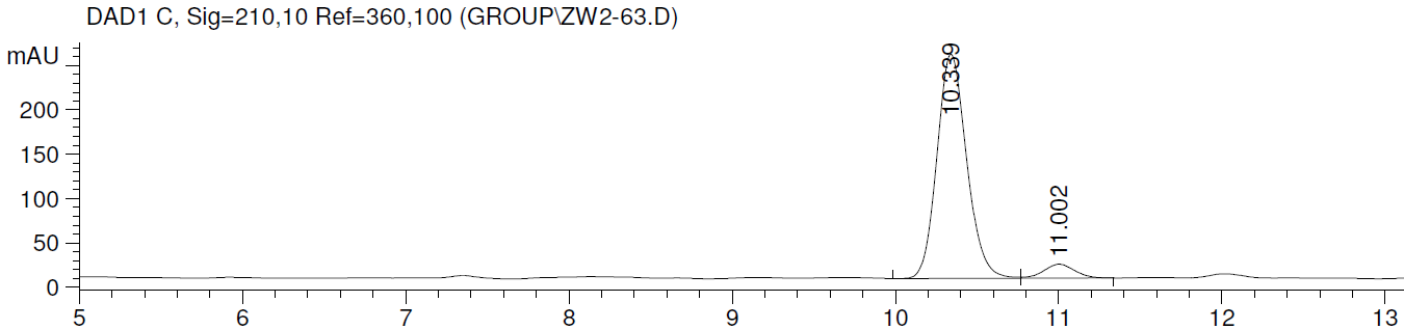
HPLC analysis: CHIRALCEL AD-H column (1% *i*-PrOH in hexane, 1.0 mL/min).

88% ee from (*R,S*)-**L1**

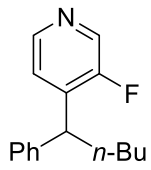



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.379 | PP | 0.1903 | 307.48566 | 24.85342 | 6.0612 |
| 2 | 11.045 | VB | 0.2038 | 4765.49805 | 361.39990 | 93.9388 |

88% ee from (*S,R*)-**L1**



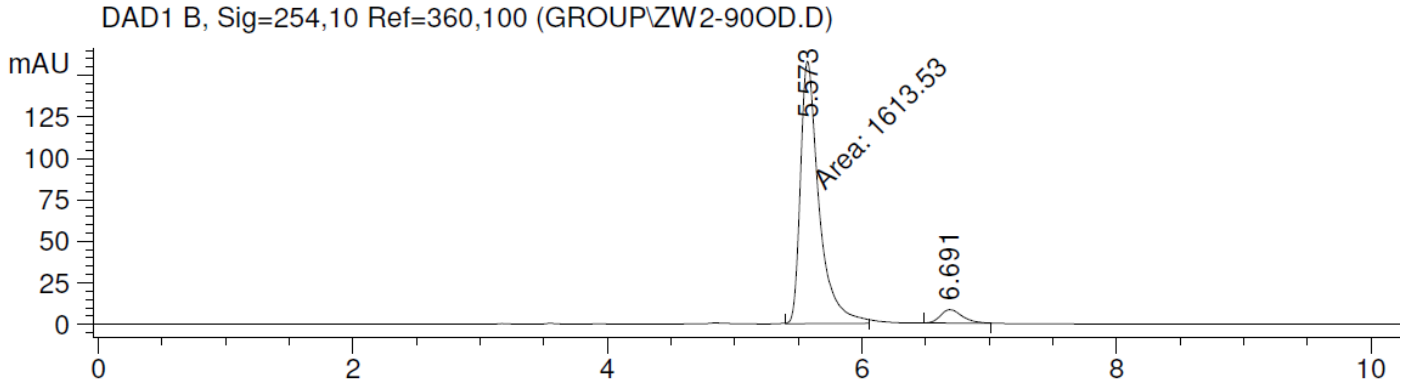

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.339 | VB | 0.1956 | 3198.76343 | 252.86923 | 93.9181 |
| 2 | 11.002 | BP | 0.2042 | 207.14505 | 15.67045 | 6.0819 |




**3-Fluoro-4-(1-phenylpentyl)pyridine (Fig. 3).**

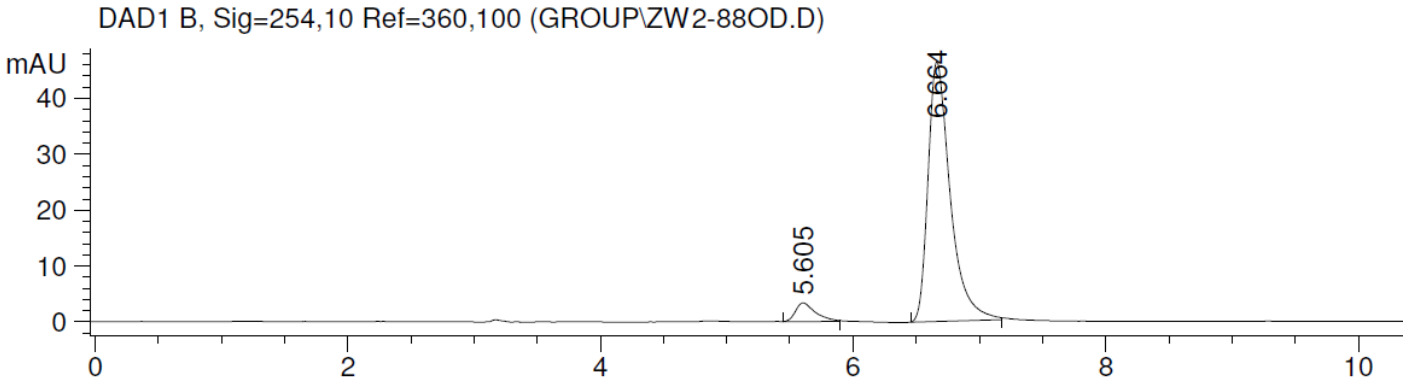
HPLC analysis: CHIRALCEL OD-H column (10% *i*-PrOH in hexane, 1.0 mL/min).

88% ee from (*R,S*)-**L1**

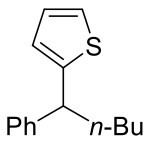



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.573 | MF | 0.1698 | 1613.53235 | 158.34892 | 94.2557 |
| 2 | 6.691 | BB | 0.1821 | 98.33431 | 8.18591 | 5.7443 |

88% ee from (*S,R*)-**L1**



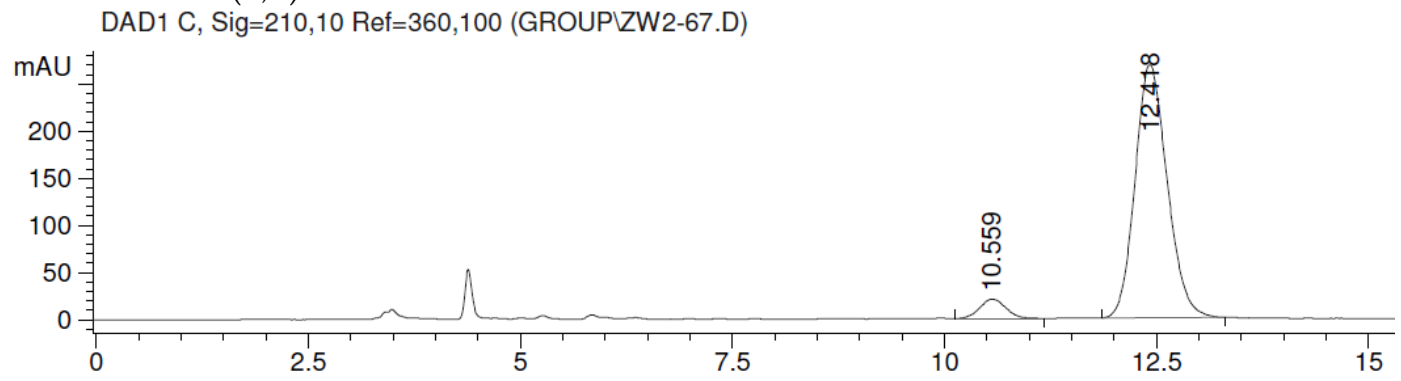

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.605 | BB | 0.1631 | 36.87300 | 3.33209 | 6.1294 |
| 2 | 6.664 | BB | 0.1817 | 564.70111 | 46.48492 | 93.8706 |




**2-(1-Phenylpentyl)thiophene (Fig. 3).**

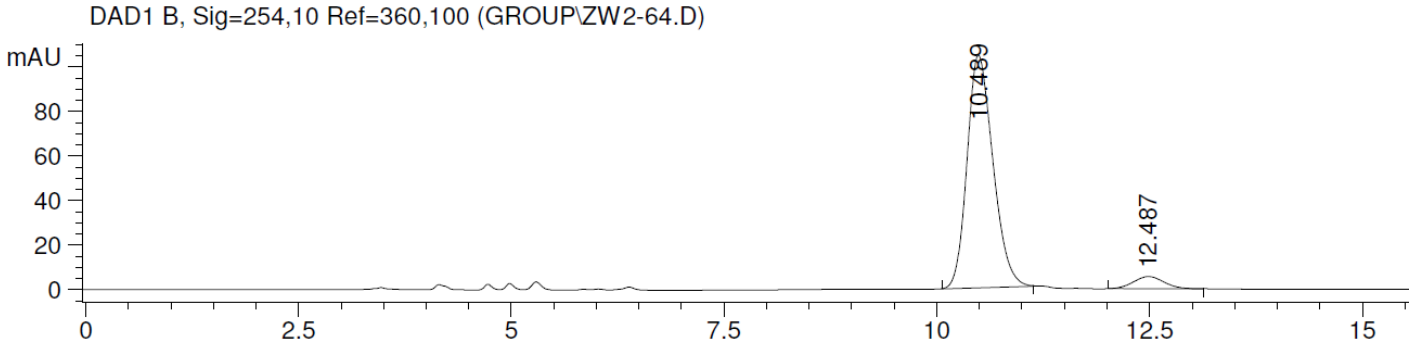
HPLC analysis: CHIRALCEL OJ-H column (5% *i*-PrOH in hexane, 1.0 mL/min).

88% ee from (*R,S*)-**L1**

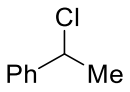



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.559 | VP | 0.3284 | 446.85883 | 20.81874 | 5.9372 |
| 2 | 12.418 | BB | 0.4034 | 7079.57373 | 268.71646 | 94.0628 |

88% ee from (*S,R*)-**L1**



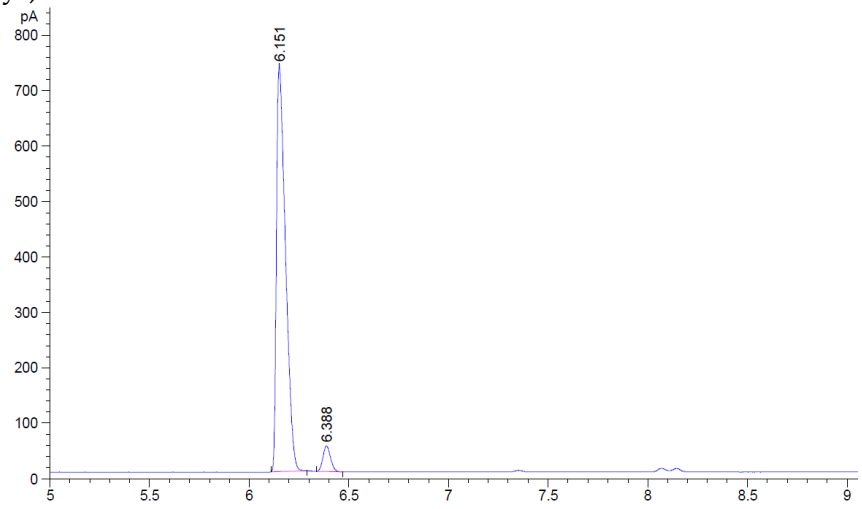

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.489 | BB | 0.3270 | 2210.75781 | 104.43446 | 94.1723 |
| 2 | 12.487 | BB | 0.3772 | 136.80814 | 5.44373 | 5.8277 |




**(1-Chloroethyl)benzene (eq 2 and 3).**

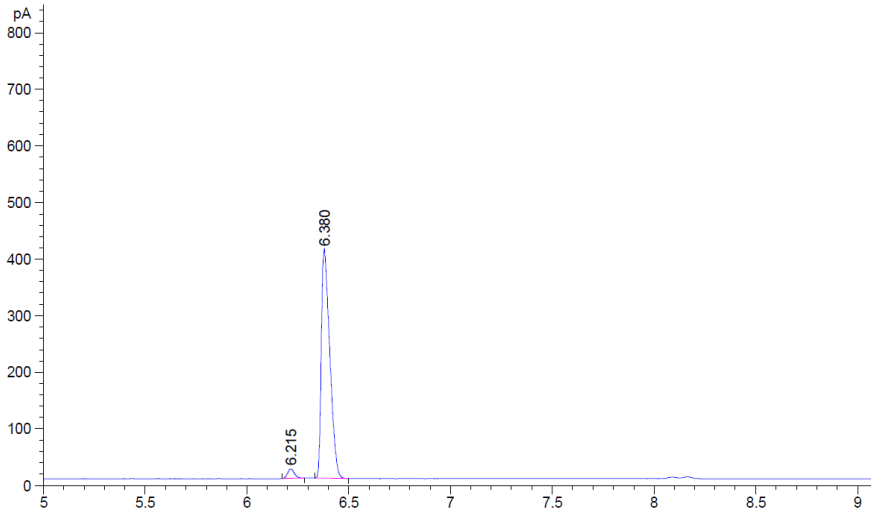
GC analysis: CHIRALDEX G-TA column (80 – 180 °C, ramp: 5 °C /min).

(*R*)-(1-chloroethyl)benzene: 90% ee




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.151 | BB | 0.0468 | 2307.55176 | 731.97400 | 94.97150 |
| 2 | 6.388 | BB | 0.0418 | 122.17901 | 46.31799 | 5.02850 |

(*S*)-(1-chloroethyl)benzene: 94% ee




| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.215 | BB | 0.0356 | 38.29222 | 16.81598 | 3.16848 |
| 2 | 6.380 | BB | 0.0438 | 1170.24463 | 403.44101 | 96.83152 |